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Determination, study and elimination of organic pollutants from surface and wastewater

PhD thesis summary

Scientific supervisor
Prof. Dr. Ion GROSU

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Keywords: organic pollutants; water decontamination; sorption; analytical methods; wastewaters

Content

Pollution issues in the aquatic environment

In recent decades, a constant increase in public awareness of the environmental protection issues has been observed both globally and locally. It is recognized that the pollution influences living organisms, humans included, both directly (by affecting their health) and indirectly (via contamination of food) [1].

Pesticides are high biologically active substances, used to control diseases, pests and weeds, with diverse chemical structure [2]. Besides the undeniable advantages which occurred with the adoption of pesticides in terms of high yields in intensive farming, evolution of agronomic techniques, increasing of food production, and quality improvement of foodstuffs, heavy drawbacks have been observed and documented on soil and aquatic environments and on human health since the early 1960s [3; 4; 5]. It is precisely those properties that make them effective against plagues that turn them into polluting agents [6]. The family of s-triazines comprises some of the most widely employed pesticides in the world. They are used as selective herbicides to control broadleaf and grassy weeds when growing many agricultural crops. Those herbicides are very persistent in the environment and their prolonged use involves risking their retention in crops and soils [7]. Phenylurea herbicides (PUHs) such as diuron, isoproturon and chlorotoluron are used in large quantities for various purposes, for examples: as herbicides in cereal crops (isoproturon and chlorotoluron), as total herbicides in agriculture or in settlements (diuron), as algicides in paintings and coatings (diuron), for renovation of sporting grounds, bowling greens and golf courses, railway easements and roadway nature strips [8]. Another important group of anthropogenic organic pollutants found in aquatic systems are the biocides [9]. They are widely used in antifouling paints on boats and static structures to prevent the growth of attached aquatic organisms, especially molluscs and algae [10]. Several studies have evaluated the toxicity of booster biocides on non-target species and found most of them to be growth inhibitors for freshwater and marine autotrophs, influencing key species like sea grasses and corals [11]. Linear alkylbenzene sulfonate (LAS) is one of the most common and used anionic surfactants in the formulation of household and laundry detergents, hand dishwashing liquids, shampoos, and other personal care products with an estimated global consumption of 2,8 milion tonnes in 1998 [12].

The most direct impact of water pollution on human health comes through drinking contaminated water, but contaminants can be absorbed through the skin and ingested from food chain as well [13]. Previous studies of the health impacts of water pollution in China have found evidence of increased rates of liver and stomach cancer due to the consumtion of water with high levels of chemicals and heavy metals [14].

The European Union has established various directives such as *Water Framework Directive (WFD) 2000/60/EC* on water quality. One of the objectives of the Water Framework Directive is to obtain a good status for rivers by 2020 in European countries and to develop water management based on river basin districts [15].

Several research studies showed that, treated wastewater, if appropriately managed, is viewed as a major component of the water resources supply to meet the needs of a growing economy. The greatest challenge in implementing this strategy is the adoption of low cost wastewater treatment technologies that will maximize the efficiency of utilizing limited water resources and ensuring compliance with all health and safety standards regarding reuse of treated wastewater effluents [16].

Considering the above mentioned, in this work, was studied the behavior of some organic pollutants in wastewater and surface water, as well as more effective ways to eliminate them. For this, have been used different methods of sample processing and a wide range of analytical techniques.

Sorption of biocides, triazine and phenylurea herbicides onto secondary sludge

The objective of the current study was to elucidate the sorption behavior of several structurally diverse emerging micropollutants including biocides, *"UV-filters",* as well as triazines and phenylurea herbicides as for most of these compounds this data is still lacking. A special focus was set on: (i) the sorption kinetics with and without using NaN_3 for inhibition of the microbial activity, (ii) the concentration dependency of sorption (sorption isotherms) and (iii) the correlation of the log K_{OW} as a measure of hydrophobicity with sludge-water distribution coefficients.

Sampling

The sludge for the laboratory batch experiments was taken in solvent-rinsed amber glass bottles from the nitrifying zone of the activated sludge treatment of a German municipal WWTP serving 300,000 population equivalents (PE). The activated sludge system is operated with a hydraulic retention time (HRT) and sludge retention time (SRT) of 12 h and 10-12 days, respectively. Wastewater treatment plant consists of a mechanical treatment (screen, grit removal and primary clarifier), a trickling filter followed by an activated sludge treatment with nitrification and denitrification, phosphate removal and a final clarification.

Sorption kinetics: sorption equilibrium and influence of sodium azide

A homogenous suspension (190mL) of the activated sludge was filled into 500 mL centrifuge bottles (polypropylene). For each sampling time point (0, 0.75, 1.5, 3.2, 6 and 24 h) three samples with 0, 0.2 and 1% NaN3 concentrations were prepared by adding 10 mL of Milli-Q water, 4 % and 20 % NaN_3 solution, respectively. Target compounds were spiked to a concentration of 10 µg/L and the samples were placed on a horizontal shaker for the different incubation times. The background concentration of the target compounds in the sludge was assessed in non-spiked controls for the first sampling point (t = 0 h). The ambient pH of the sludge was stable (6.8 ± 0.2) throughout the incubation period. After the defined exposure time, the sludge was centrifuged (15 min, 3640 g) and the supernatant was stored at 4 °C for solid-phase extraction (SPE). The solid sludge particles were freeze-dried for micropollutant analysis and the water content f_{water} ($L/g_{dw\ sludge}$) was determined by the difference of the sludge wet and dry weight before and after freeze-drying, respectively.

Freundlich sorption isotherms

The experimental set-up and sludge characteristics were similar to the equilibrium experiments described above. The Freundlich isotherms were determined by spiking the target compounds into 200 mL of secondary sludge to a concentration of 0.1, 0.3, 1, 3, 10 and 30 µg/L. All samples were prepared in duplicate and incubated for 1.5 h to ensure sorption equilibrium. Non-spiked samples were analyzed at the beginning and at the end of the incubation period to assess the natural background concentration. Filtered (Whatman, GF6) samples of the supernatant of centrifuged sludge were spiked to a concentration of 10 µg/L and served as controls for any compound losses due to sorption to the glass vessels.

Analytical methods

The detection was performed using reversed-phase liquid chromatography (Synergi Fusion-RP, 150 x 3 mm, 4 µm, Phenomenex, Aschaffenburg, Germany) coupled to electrospray mass spectrometry operated in the positive and negative ionization mode.

All target analytes were quantified using an internal standard calibration and the limit of quantification (LOQ) was defined as the second lowest calibration point in the regression as long as the calculated signal to noise ratio (S/N) of the analytes in the native sample extracts was >10 for the first transition (MRM 1) used for quantification and >3 for the second transition (MRM 2) used for confirmation. The retention time, MRM transitions and corresponding MS parameters of triazines and phenylurea herbicides are presented in **Table 1**.

Table 1. Retention time, precursor ion, product ions and MS parameters used for LC-MS/MS detection of triazines and phenyl urea herbicides

Compound	Retention time (min.)	MRM1	MRM2	DP* (V)	CE** MRM1/MRM2 (eV)	CXP*** MRM1/MRM2 (V)
Fluometuron	11.7	233 → 72	233 → 46	80	38/35	10/10
Chloroxuron	14.6	291 →72	291 → 218	90	42/35	10/10
Linuron	13.9	249 → 160	249 → 182	80	23/22	10/10
Monolinuron	11.9	215 → 126	215 → 99	60	24/46	10/10
Neburon	15.7	275 → 88	275 → 114	85	23/20	10/10
Monuron	10.5	199 → 72	199 → 126	90	39/36	10/10
Methabenzthiazuron	11.3	222 → 165	222 → 150	50	29/45	14/14
Atrazine	11.5	216 → 174	216 → 132	70	27/34	19/9
Atrazine-d_5	11.4	221 → 179	223 → 181	60	23/23	10/10
Simazine	10.2	202 → 132	202 → 124	85	26/25	10/10
Cyanazine	10.3	241 → 214	241 → 104	120	23/42	10/10
Propazine	12.9	230 → 146	330 → 188	35	31/25	15/15
Ametryn	12.2	228 → 186	228 → 68	85	26/54	12/12
Prometryn	13.5	242 → 158	242 → 200	85	33/27	12/12
Prometon	11.1	226 → 142	226 → 184	90	33/32	10/10

*DP = Declustering potential, **CE = Collision energy, ***CXP = Collision cell exit potential

Method validation

In general, selected compounds can be analyzed with an acceptable accuracy in groundwater, surface water and raw and treated wastewater with ESI as well as APCI

The effect of pH on the extraction efficiency was tested in a range of pH 5–8. Due to diversity of target analytes with a broad range of pKa values, no optimal pH value for all analytes could be found. However, for most analytes no effect was observed or was statistically insignificant. To ensure reproducible recoveries, the pH was adjusted to 6 as a compromise for the selected analytes.

It also examined the recovery for all analytes in the current study to confirm the functionality of the method. The relative recoveries were determined as the ratio of the spiked concentration and the quantified concentrations at a spiking level of 2 µg/L and 4 µg/g$_{\text{dw sludge}}$ in the aqueous phase and freeze-dried sludge, respectively (dublicate measurements). The relative recoveries were in an acceptable range of 70–130 %. The results are reported in **Table 2.**

Table 2. Relative recovery (%) and limit of quantification (LOQ) determined for the aqueous phase and the freeze dried sludge

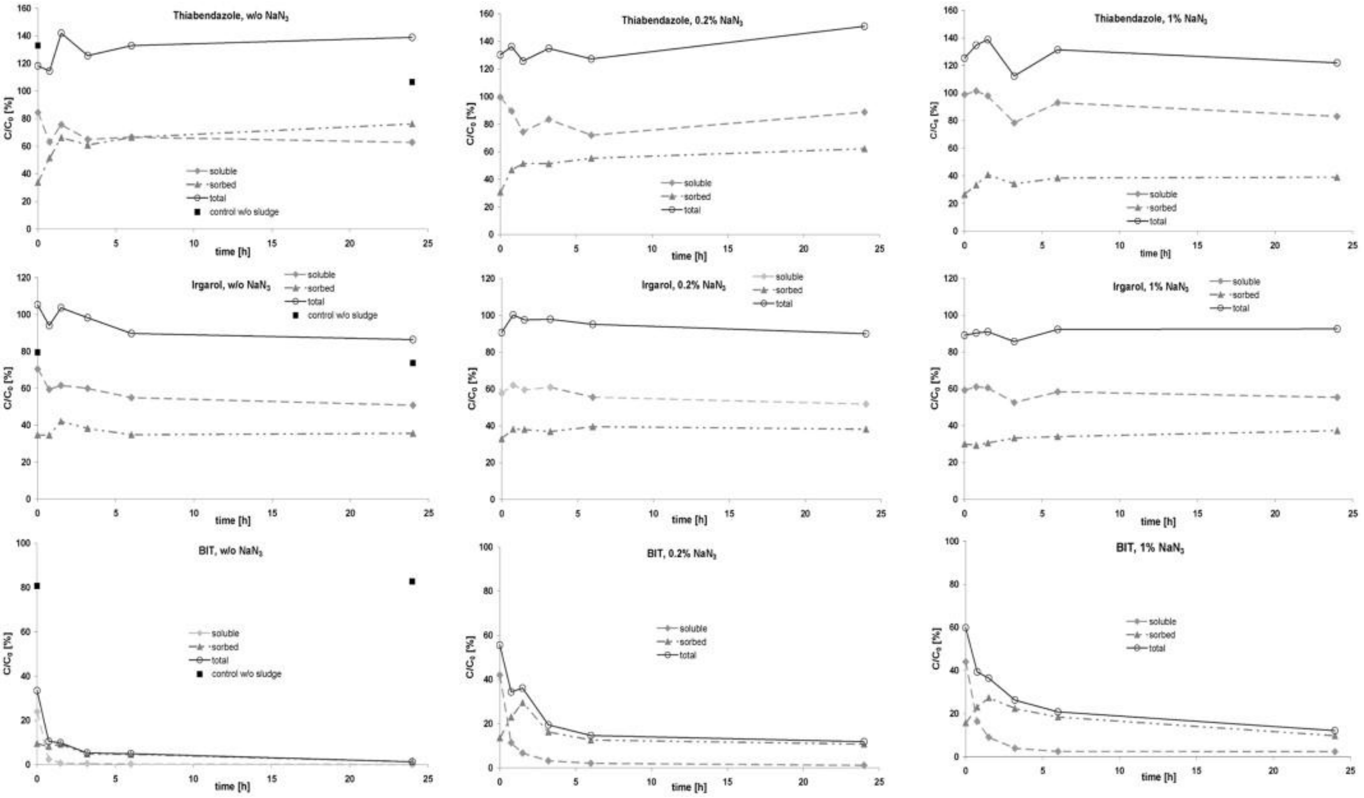
Compound	Aqueous phase		Solid phase		Surrogate standard used
	Rel. Rec. (%)	LOQ (ng/L)	Rel. Rec. (%)	LOQ	
Phenylurea herbicides					
Diuron	79	2.5	90	2.5	Diuron-d$_6$
Isoproturon	91	5.0	98	5.0	Isoproturon-d$_6$
Fluometuron	91	2.5	93	2.5	Diuron-d$_6$
Chloroxuron	79	2.5	49	2.5	Diuron-d$_6$
Linuron	88	2.5	53	2.5	Diuron-d$_6$
Monolinuron	97	2.5	85	2.5	Diuron-d$_6$
Neburon	85	2.5	59	2.5	Diuron-d$_6$
Monuron	88	5.0	108	5.0	Diuron-d$_6$
Methabenzthiazuron	90	2.5	111	2.5	Diuron-d$_6$
Triazines					
Atrazine	94	2.5	93	2.5	Atrazine-d$_5$
Simazine	98	2.5	113	2.5	Atrazine-d$_5$
Cyanazine	53	5.0	97	5.0	Terbuthylazine-d$_5$
Propazine	97	2.5	103	2.5	Terbuthylazine-d$_5$
Terbuthylazine	89	2.5	98	2.5	Terbuthylazine-d$_5$
Terbutryn	83	2.5	79	2.5	Terbutryn-d$_5$
Irgarol	91	2.5	98	2.5	Terbutryn-d$_5$
M1	89	5.0	117	5.0	Terbutryn-d$_5$
Ametryn	108	2.5	124	2.5	Terbuthylazine-d$_5$
Prometryn	121	2.5	132	2.5	Terbuthylazine-d$_5$
Prometon	118	2.5	122	2.5	Terbuthylazine-d$_5$
Biocides					
Mecoprop	111	10	101	10	Mecoprop-d$_3$
Propiconazole	84	2.5	96	5.0	Propiconazole-d$_5$
Tebuconazole	99	2.5	110	5.0	Tebuconazole-d$_6$
Imazalil	94	5.0	88	5.0	Imazalil-d$_5$
Carbendazim	87	2.5	88	5.0	Carbendazim-d$_4$
Thiabendazole	92	2.5	107	2.5	Thiabendazole-d$_6$
Dimethomorph	93	5.0	95	5.0	Terbuthylazine-d$_5$
Fenpropimorph	84	2.5	106	2.5	Imazalil-d$_5$
Tridemorph	64	20	93	50	Imazalil-d$_5$
BIT	92	100	82	100	Propiconazole-d$_5$
OIT	102	5	54	10	Propiconazole-d$_5$
DMST	90	10	86	10	Isoproturon-d$_6$
DMSA	111	25	119	25	Mecoprop-d$_3$
Triclosan	96	10	100	10	Triclosan-^{13}C$_6$
Triclocarban	107	2.5	99	2.5	Triclocarban-^{13}C$_6$
Chlorophene	95	5.0	106	10	Triclosan-^{13}C$_6$
UV-filters					
BZP-1	105	2.5	83	2.5	Diuron-d$_6$
BZP-2	113	2.5	99	2.5	Diuron-d$_6$
BZP-3	90	25	108	25	Thiabendazole-d$_6$
BZP-4	106	5.0	103	5.0	Mecoprop-d$_3$
PBSA	110	5.0	118	5.0	Terbutryn-d$_5$

Results and discussion

Sorption kinetics

Figure 1 shows exemplarily the sorption kinetics of the biocides irgarol, thiabendazole and 1,2-benzisothiazolin-3-one (BIT) to secondary sludge with and without adding NaN_3 by comparing the ratio of the measured sorbed, soluble and total concentration to the spike concentration of 10 µg/L. The total analyte concentration is calculated as the sum of the soluble and sorbed concentrations.

Figure 1. Ratio (%) of sorbed, soluble and the total concentration to the spike concentration of 10 µg/L over time for three selected with and without addition of NaN_3 for microbial activity inhibition. The background concentrations as well as the water content of the sludge were assessed and considered for the calculation.



At least in the NaN_3 amended samples the sorbed concentration was constant after 1.5 h, indicating that sorption equilibrium was reached except for BIT and 2-n-octyl-4-isothaizolin-3-one (OIT) being subject of significant biodegradation.

For 18 of 27 analytes the mass balance in sludge amended samples as well as in filtered control samples without sludge was in an acceptable range of 100 ± 30% indicating a good analytical method performance as well as no significant losses by degradation and volatilization.

For 18 out of 27 analytes the addition of NaN_3 had a distinct influence on the sludge-water distribution. While for the triazines, such as irgarol, the ratio of sorbed and soluble concentration was comparable with different NaN_3 concentrations, the sorbed concentration was lower for most analytes including thiabendazole and diuron.

Further investigations are needed to fully understand the mode of action of NaN_3 on the sorption kinetics and chemical analysis, but the results confirmed that NaN_3 can have a negative impact on the reliability of sorption experiments. However, except for the fast degrading isothiazolones BIT and OIT, the distribution of the analytes between sludge and water phase, i.e. the $K_{d,sec}$ values, did not significantly change in the period from 1.5 to 6 h of incubation without using NaN_3.

Freundlich isotherms

Isotherm experiments were performed for all analytes for which the sorption kinetics were examined except for BIT and OIT, as for these two isothiazolinones sorption equilibria were not attained due to rapid biodegradation. Moreover, seven additional triazines and seven phenylurea herbicides were included in the isotherm studies. Based on the results from the sorption kinetics, sorption isotherm experiments were conducted without adding NaN_3 using an equilibrium time of 1.5 h. Freundlich isotherms were determined by linear regression of the logarithmized sorbed and soluble concentrations for all compounds for which the concentrations were above the limit of quantification for more than 3 spiking levels.

Conclusions

Within the present study the sorption of 41 micropollutants to activated sludge was investigated. For 27 contaminants, sludge-water distribution coefficients and their concentration dependency was determined for the first time. Both are major prerequisites for assessing their fate in WWTPs and thus their potential release into the environment via treated wastewater or via sludge amendment to agricultural land.

Furthermore, the results of the present study imply important aspects for performing sorption experiments with fresh activated sludge. NaN_3 has been shown to be inappropriate for the deactivation of fresh sludge due to (i) insufficient inhibition of microbial degradation and (ii) its influence on the sludge-water distribution. To the best of our knowledge, this is the first study confirming that increasing NaN_3 concentrations can lead to decreasing compound amounts sorbed to activated sludge. In addition, the results show that the deactivation of sludge is not a prerequisite if biodegradation does not hinder the attainment of sorption equilibria. However, quantification of the analytes in both sludge and aqueous phase is crucial if biodegradation cannot be excluded, since analyzing only the dissolved concentration would lead to increased distribution coefficients.

The Freundlich model was shown to be appropriate to describe the sorption behavior of various micropollutants in contact to secondary sludge. Since for many compounds the Freundlich exponents were close to 1 and thus $Kf \approx Kd$, the linear model can be used in most cases for a rapid determination of sludge-water distribution coefficients. For the linear approach concentrations should be as close as possible to real concentrations in full-scale WWTPs.

The determination of the linear alkylbenzene sulfonate isomers in water samples by gas-chromatography/mass spectrometry. The use of zeolites in their removal and other organic pollutants

The linear alkylbenzene sulfonates (LASs) molecules contain an aromatic ring sulfonated at the para position, which is attached to a linear alkyl chain at any position except the terminal carbons. The LASs are the most used anionic surfactants in various industrial, household and commercial applications [17; 18].

The global consumption of LAS was estimated to be about 2.2×109 kg in 2000 and 2.5×109 kg in 2002. The European consumption of LAS was about of 4.3×108 kg in the year 2005. [19].

This chapter discusses the mass spectra, structural correlation and distribution of 20 identified LASs compounds in samples collected in compartments of WWTP containing different amounts of zeolites, by electron impact-mass spectrometry technique (EI-MS), and their adsorbtion on various amounts of zeolite. It was also studied, the proposed mechanism of formation of the diagnostic ions obtained by EI-MS and the distribution of individual isomers from four homolog series C10-, C11-, C12- and C13-LAS. The compounds were analyzed as methyl esters derivatives. The structural details (chain length, position of aromatic ring, elution time and used symbols) are presented in **Table 3**.

Table 3. Structure of investigated compounds: $C_kH_{k+1} – CH(C_mH_{m+1}) – C_6H_6 – SO_2 – O – CH_3$, elution time and used symbols.

No.	n	k	m	M_w	Elution time (min)	Symbol
1	10	1	8	312	23.29	10 (1,8)
2		2	7		22.35	10 (2,7)
3		3	6		21.81	10 (3,6)
4		4	5		21.57	10 (4,5)
5	11	1	9	326	25.37	11 (1,9)
6		2	8		24.41	11 (2,8)
7		3	7		23.84	11 (3,7)
8		4	6		23.55	11 (4,6)
9		5	5		23.49	11 (5,5)
10	12	1	10	340	27.41	12 (1,10)
11		2	9		26.43	12 (2,9)
12		3	8		25.86	12 (3,8)
13		4	7		25.52	12 (4,7)
14		5	6		25.41	12 (5,6)
15	13	1	11	340	29.38	13 (1,11)
16		2	10		28.43	13 (2,10)
17		3	9		27.81	13 (3,9)
18		4	8		27.50	13 (4,8)
19		5	7		27.34	13 (5,7)
20		6	6		27.32	13 (6,6)

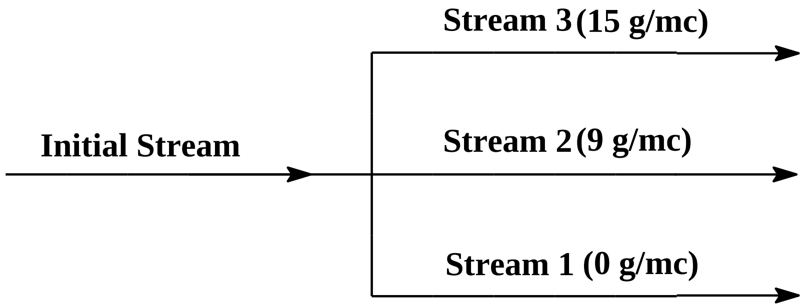
n: number of carbon in alkyl chain; k, m: number of carbon atoms of every alkyl branch
($n = k + m + 1$)

Experimental

Sampling and sample preparation

The samples were taken from a WWTP with three different lines (P1, P2 and P3) containing different amounts of zeolites: basin **1** (0 g/m^3, reference site); basin **2** (9 g/m^3, maintain 5.0 % concentration of zeolite in the activated sludge); basin **3** (15 g/m^3 maintain 7.5 % concentration of zeolite in the activated sludge.). The simplified scheme of experimental WWTP is shown in **Figure 2.**

Figure 2. The simplified scheme of zeolite dosing points



GC/MS analysis

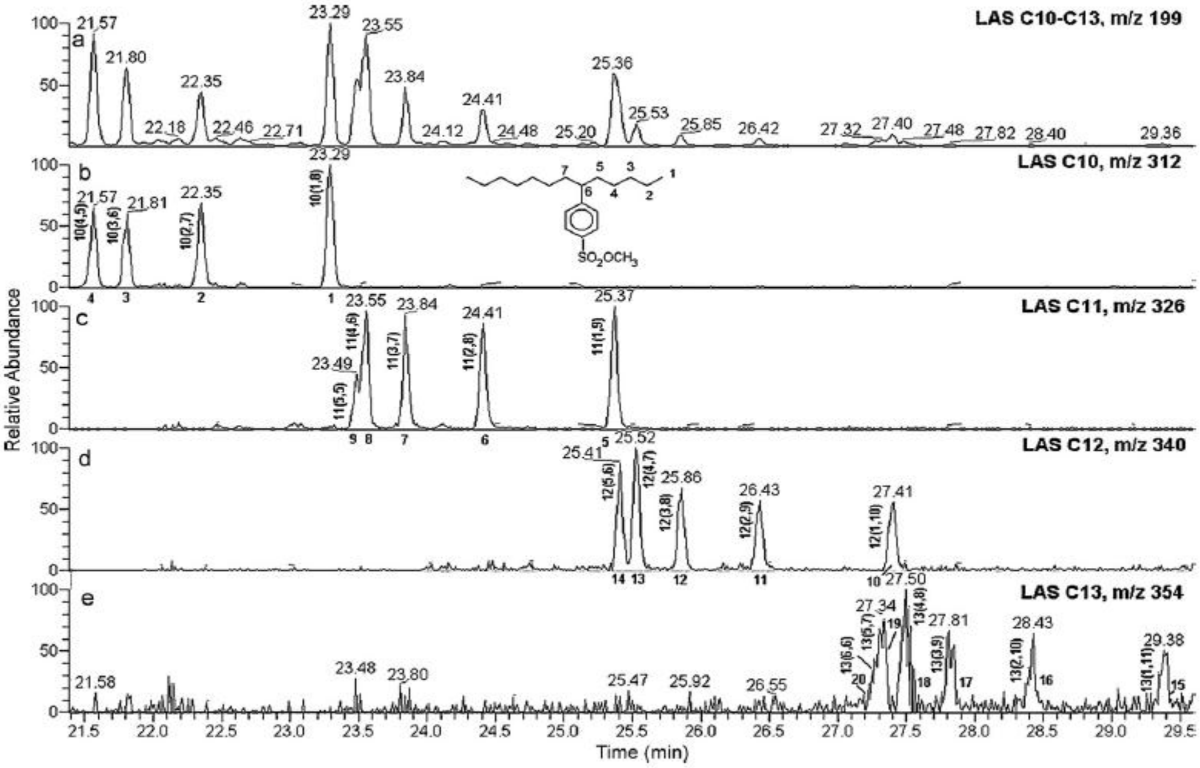
The GC/MS analyses were performed using a Thermo Electron Polaris Q mass spectrometer operating in EI mode at 70 eV. The source temperature was 230 ºC and emission current 300 μA. The gas chromatograph was equipped with a capillary column HP-5MS (30mm × 0.25mm) with 0.25 μm film thickness. The temperature was programmed from 90 ºC (1min) to 120 ºC at 10 ºC/min and than to 200 ºC at 3.5 ºC/min and than to 315 ºC at 5 ºC/min (keeping this temperature for 11 min). The injector temperature was of 250 ºC and 2 μl of sample was injected by splitless technique, with split flow 50 ml/min and splitless time 1 min.

Results and discussions

Mass spectra of LASs

The molecular distribution of the isomers in a sample collected fromWWTP is described by the characteristic ion profiles (m/z 199, 312, 326, 340 and 354) after methylating, and is shown in **Figure 3**. The ion at m/z 199 is a main peak in all mass spectra, and the ions at m/z 312, 326, 340 and 354 are the molecular ions of homologues series C_{10}-LAS, C_{11}-LAS, C_{12}-LAS and C_{13}-LAS, respectively. All isomers are completely separated except the compound **11** (5,5) relative at **11** (4,6) and **13** (5,7) relative at **13** (6,6).

Figure 3. GC/MS chromatogram of LAS isomers from a real sample: (a) m/z 199 (main ion for LASs), (b) 312 (M^{*+} for C_{10}-LAS), (c) 326 (M^{*+} for C_{11}-LAS), (d) 340 (M^{*+} for C_{12}-LAS), and (e) 354 (M^{*+} for C_{13}-LAS)



Study of LAS removal in WWTP using absorption on zeolites

The zeolite selected for sewage treatment as additive in the sedimentation basin was Szedimentin-MW (GEOPRODUCT KFT. 3909 MAD, Hungary) with chemical composition of mineral component known. The analyzed samples were taken from the compartments of WWTP as described in previous section. The amount of each LAS compounds was measured from GC/MS base peak area. The removal rate was obtained by comparison of concentration in different compartments, with the concentration in a reference line (line without zeolites). The results are shown in **Table 4**.

Table 4. LAS concentration (ng/L) measured in the WWTP compartments and removal rate relative to reference line.

Phenyl position	Compound concentration (ng/L)			Removal rate (%)	
	P1	P2	P3	R(P2)	R(P3)
C_{10}-LASs (M = 312)					
(5)	653 ± 6.2	454 ± 3.6	283 ± 2.1	30.5 ± 2.8	56.7 ± 11.1
(4)	516 ± 4.8	386 ± 3.4	247 ± 2.5	25.2 ± 3.8	52.1 ± 2.8
(3)	606 ± 5.3	463 ± 4.2	351 ± 3.2	23.6 ± 3.4	42.1 ± 6.3
(2)	798 ± 6.1	608 ± 6.2	455 ± 4.3	23.8 ± 2.3	42.9 ± 5.0
				Mean = 25.9 ± 2.8	Mean = 48.8 ± 6.2
C_{11}-LASs (M = 326)					
(6)	220 ± 2.9	152 ± 7.3	110 ± 5.3	31.5 ± 4.0	50.0 ± 3.8
(5)	510 ± 4.2	372 ± 4.6	270 ± 8.3	27.1 ± 2.2	47.1 ± 5.0
(4)	435 ± 4.7	345 ± 8.1	220 ± 6.4	20.6 ± 3.0	49.4 ± 5.4
(3)	477 ± 3.8	330 ± 7.6	250 ± 5.1	30.8 ± 2.7	47.6 ± 5.9
(2)	525 ± 6.1	417 ± 4.2	395 ± 7.3	20.6 ± 1.4	49.5 ± 4.1
				Mean = 26.1 ± 2.6	Mean = 48.7 ± 3.8
C_{12}-LASs (M = 340)					
(6)	185 ± 7.1	128 ± 8.1	86 ± 4.3	30.1 ± 2.4	53.5 ± 9.6
(5)	232 ± 13.8	159 ± 7.7	103 ± 8.6	31.4 ± 3.2	55.6 ± 8.2
(4)	182 ± 5.4	125 ± 6.7	94 ± 4.7	31.3 ± 2.8	48.3 ± 4.3
(3)	124 ± 10.1	93 ± 6.4	68 ± 3.5	25.0 ± 3.7	45.2 ± 4.5
(2)	134 ± 9.6	98 ± 4.9	63 ± 6.3	26.8 ± 2.8	52.0 ± 6.7
				Mean = 28.9 ± 2.9	Mean = 50.9 ± 6.6
C_{10} + C_{11} + C_{12}				Mean = 26.9 ± 2.7	Mean = 49.3 ± 5.5

P1: reference line (no zeolites); **P2**: line with 9 g/m^3; **P3**: line with 15 g/m^3. The compounds from homologue series C_{13}-LAS were not measured.

The average removal rates obtained were 26.9 % for a zeolite concentration of 9 g/m^3 and 49.3 % for 15 g/m^3. The values were obtained by comparison with quantity from reference line (no zeolites) and are closed to those reported in other studies on LAS removal from wastewater, by physical processes (e.g. 30–35% by sorption and sedimentation). The average removal values of C_{10}-, C_{11}- and C_{12}-LAS groups show a better absorption for longer LAS (C_{12}-LAS). No discrimination was seen for isomers in the same homologue series.

Study of organic pollutants removal using zeolites

Besides linear alkylbenzene sulfonates (LASs) isomers removal from wastewater treatment plants, was also studied the removal efficiency of some organic pollutants from different classes of interest: antioxidants (BHA and BHT), triazines (Prometon, Atrazine, Propazine, Ametryn), phenylurea herbicides (Diuron, Isoproturon), musk fragrances (Galaxolide and Tonalide), antibacterial agent (Triclosan), antiepileptic drug (Carbamazepine). The compounds was separated using gas chromatography (GC) and quantified with mass spectrometry (MS). The organic pollutant concentrations in the WWTP compartments are presented in **Table 5**.

Table 5. Concentration of antioxidants (1,2), triazines (3-6), phenyl urea herbicides (7,8), fragrances (9), antimicrobials (10) and antiepileptic drugs (11) in ng/l. The symbol (*) is for concentration under LOQ, (**) the symbol BHA and BHT denoted the compounds Buthylhydroxyanisole and Buthylhydroxytoluene respectively.

Nr Crt	Compound	LOQ (ng/L)	Day 1			Day 2			Day 3		
			P1	P2	P3	P1	P2	P3	P1	P2	P3
1	BHA**	30	717	825	413	866	945	475	749	709	714
2	BHT**	30	343	220	88	269	215	137	237	196	206
3	Prometon	7	*	*	*	*	*	*	*	*	*
4	Atrazin	40	*	*	*	*	*	*	*	*	*
5	Propazin	13	*	*	*	*	*	*	*	*	*
6	Ametrin	30	*	*	*	*	*	*	*	*	*
7	Diuron	20	*	*	*	*	*	*	*	*	*
8	Isoproturon	7	*	*	*	*	*	*	*	*	*
9	Tonalide	15	349	150	159	251	199	154	199	182	144
10	Triclosan	7	264	476	215	459	505	288	472	531	254
11	Carbamazepine	10	77	77	112	114	105	113	37	44	58

Conclusions

In samples collected from a sewage treatment system was detected a number of 20 compounds from LASs family. The EI mass spectrum of homologue series C_{10}-, C_{11}-, C_{12}- and C_{13}-LAS as methyl esters derivatives, strongly depends on the position of branched carbon. The main ions observed in the mass spectra of LAS isomers, produced by simple fission processes are of type: $[M-C_iH_{2i+1}]^+$. The structure of compounds can be obtained by comparing the relative intensity of the ion produced by rearrangement and fission processes. The ion corresponding to bond fission adjacent to branched carbon (i =m and i = k) can be recognised from the ratio of ions (A + 1)/A. The ratio is more than 30%, due to the ions produced by rearrangement processes.

The molecular distribution of LAS isomers in water samples can be described by the profile of the characteristic ion chromatograms (m/z 199 as common ion for all compounds and molecular ion 312, 326, 340 and 354 corresponding to each homologue series).

The LASs compounds detected in WWTP contain chains with the number of carbon atom between 10 and 13, having concentration of: 47% (C_{10}-LAS), 40% (C_{11}-LAS), 11% (C_{12}-LAS) and 2% (C_{13}-LAS). The measured removal of 14 compounds depends on zeolite amount. The average removal rate was 26.9 % (for 9 g/m^3) and 49.3 % (for 15 g/m^3). A positive discrimination was observed in the removal process of C_{12}-LAS relative to C_{10}-LAS and C_{11}-LAS chain homologues.

Regarding the studied organic pollutants, was observed a removal efficiency of 19 % (with some exceptions) in the line with cu 9 g/m^3 zeolite and 31 % in the line with 15 g/m^3 zeolite. To increase the efficiency of removal we observe that is good to use a big amount of zeolite (> 15g/mc), added at the start of the bioreactor. In all situation carbamazepine removal was 0%.

The studied wastewaters originate main from domestic activity. This is the explanation of the fact that in all samples, pesticides classes (triazines and phenylurea herbicides) were below detection limits.

Inexpensive adsorbents derived from coffee grounds for the treatment of wastewater

Monuron (3-(4-chlorophenyl)-1, 1-dimethylurea), a herbicide and phenylurea derivative, is widely used because of its inhibition of photosynthesis. Its persistence in the environment is rather high (approximately ten months). The relatively long lifetime suggests that there is a risk of water contamination [21; 22].

Soluble forms of metals have raised increasing concerns in recent years. The excessive release of metals from industrial wastewater (mining, electroplating, metal processing, textile, battery manufacturing, pigment manufacture, printing, tanneries, petroleum refining, and paint manufacture) into the environment is a major concern worldwide [23]. Most metal ions become harmful when their concentration exceeds a certain level, which depends on the sensitivity of the consuming organism. Strict environmental protection legislation and public environmental concerns have led to the search for techniques to remove metals from industrial wastewater [24].

In this study was investigate the feasibility of using coffee residue with minimal processing and pyrolyzed at 500 ºC as natural biosorbents for the removal of monuron and trace metals from aqueous solution.

Analytical Methods

The determination of monuron was performed on Accela HPLC system from Thermo Scientific (Bremen, Germany) that included a photodiode array detector, an autosampler equipped with a column oven and a tray compartment cooler, and a quaternary pump with a built-in solvent degasser, all controlled by Xcalibur software. The separations were achieved using reversed phase chromatography with gradient elution.

Trace metals analysis was performed by inductively coupled plasma – mass spectrometry (ICP-MS). For each sample, three replicates were measured in order to assure quality control. Calibration curves were obtained with aqueous standards for all analytes and the linearity of six points was considered to be acceptable ($R^2 > 0.999$).

Characterization of Materials

Total surface area (S_t), pore volume (V_p), and pore radius (R_m) of samples were obtained from nitrogen adsorption – desorption isotherms (measured at – 196 ºC), using the Brunauer - Emmett–Teller (BET) model for S_t determination and Horvath – Kawasoe method for V_p and R_m. The isotherms were recorded using a Sorptomatic 1990 apparatus (Thermo Electron Corporation).

Figure 4. The adsorption – desorption isotherms and medium pore radius (R_m) distribution for activated carbon

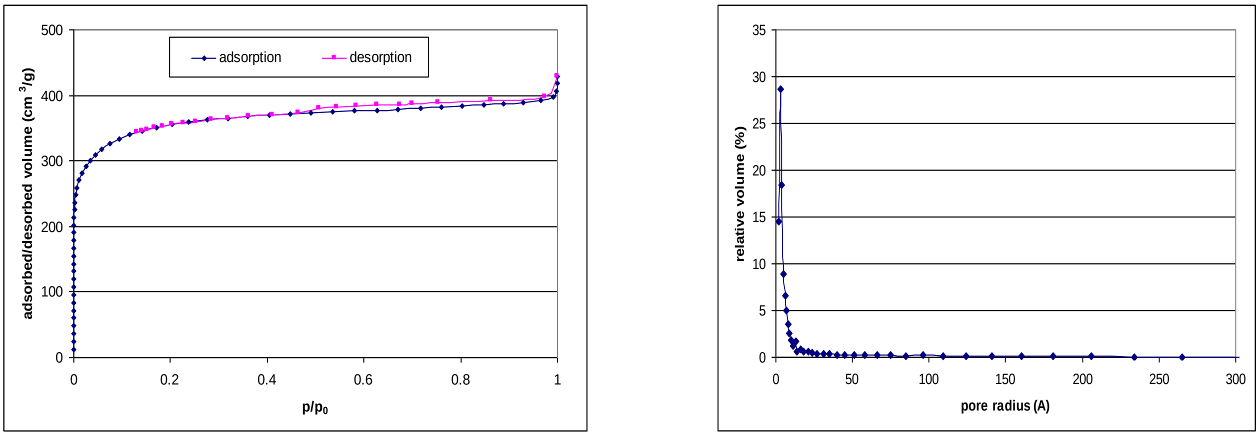


Figure 5. The adsorption – desorption isotherms and medium pore radius (R_m) distribution for coffee waste with minimal processing

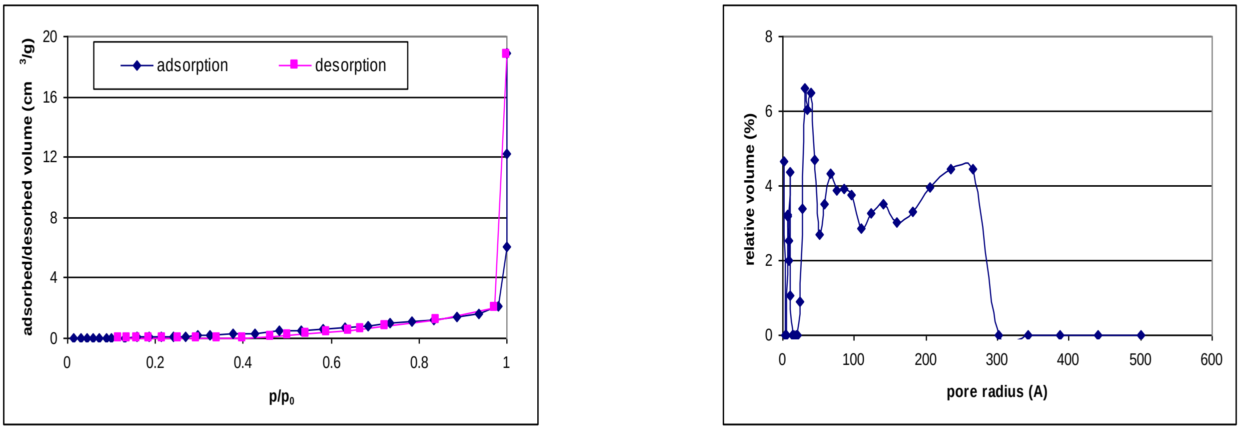
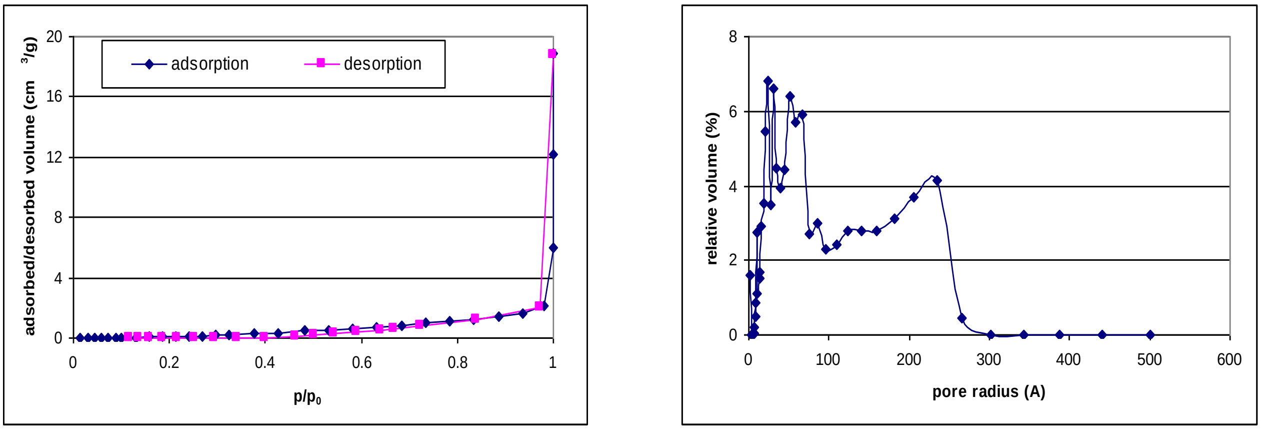


Figure 6. The adsorption – desorption isotherms and medium pore radius (R_m) distribution for pyrolyzed coffee waste



Adsorption Measurements

All adsorption experiments were performed in 250 mL brown glass vials at room temperature and constant pH. Ultrahigh quality water was used to prepare all solutions. For the adsorption of the herbicide, four 100 ml samples containing 10 μg·ml^{-1} monuron were prepared. The first sample had no coffee waste adsorbent (Blank), the second contained 100 mg of coffee grounds with minimal processing, the third had 100 mg of pyrolyzed coffee grounds, and the fourth had 100 mg of activated carbon as a reference.

For the adsorption of metals, four samples of 100 μg·L^{-1} standards of Mixture 1 and Mixture 2 were prepared. The adsorbent dosage was increased to examine the effect of mass on the adsorption of metals (**Table 6**). After equilibration for 24 h, the suspensions were passed through 0.45 μm GF/C filters (Whatman, UK) and analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

Table 6. Sample preparation for adsorption of metals from Mixture 1: Ag, Bi, Co, Ga, In, Ni, and U and Mixture 2: Pd, Pt, Sb, Sn, and Ir with coffee grounds

Mixture 1 (100 μg/L)				**Mixture 2 (100 μg/L)**			
Blank	1a	1b	1c	Blank	2a	2b	2c
no coffe waste	100 mg coffe waste	200 mg coffe waste	300 mg coffe waste	no coffe waste	100 mg coffe waste	200 mg coffe waste	300 mg coffe waste

Results and discussions

Adsorption of Monuron

The results for the adsorption of monuron on the adsorbents are shown in **Table 7**. The concentration of monuron in the aqueous phase was calculated from the calibration curves, following adsorption, by measuring the corresponding peak areas. The solid phase extraction (SPE) yield of monuron was 91.4%.

The results showed that the sorption capacity of activated carbon, the reference material, was high (9.04 $mg \cdot g^{-1}$). Initially, the adsorption of monuron on coffee waste was low. The removal efficiencies of 18.9% with unpyrolyzed coffee waste and 23.9% with pyrolyzed coffee waste were low compared to the values for activated carbon (90.4%).

Table 7. Adsorbed monuron ($mg \cdot g^{-1}$) and the removal efficiency of adsorbents (1 – Blank (no coffe waste); 2 – 100 mg coffe waste; 3 – 100 mg pyrolyzed coffe waste; 4 – 100 mg activated carbon).

Sample number	Monuron			
	Initial concentration (C_0) ($\mu g \cdot ml^{-1}$)	**Concentration at equilibrium time (C_t) ($\mu g \cdot ml^{-1}$)**	**Concentration of monuron (adsorbed) (q_e) ($mg \cdot g^{-1}$)**	**Removal (%)**
1	10	-	-	-
2	10	8.11	1.89	18.9
3	10	7.61	2.39	23.9
4	10	0.96	9.04	90.4

Adsorption of Metals

The metal concentrations from Mixtures 1 and 2 following adsorption measurements are provided in **Tables 8** and **9**, with the standard deviations and correlation coefficients. The adsorption of some trace metals on unpyrolyzed coffee grounds was more efficient than for monuron.

Table 8. Metal concentrations from Mixture 1 in the aqueous phase (μg·L^{-1}); standard deviations (SD); correlation coefficients from calibration curves (R^2).

Analyte	Metal Concentrations ± Standard Deviations				Correlation Coefficients
	Blank no coffe waste μg/L	Sample 1a 100 mg coffe waste μg/L	Sample 1b 200 mg coffe waste μg/L	Sample 1c 300 mg coffe waste μg/L	
Ni	75.0 ± 0.37	63.2 ± 5.11	60.5 ± 3.26	48.1 ± 0.09	0.99925
Co	75.1 ± 0.6	63.3 ± 4.93	59.6 ± 3.57	48.6 ± 1.16	0.99908
Ga	90.9 ± 1.27	76.8 ± 5.22	67.5 ± 3.17	48.0 ± 0.81	0.99934
Ag	63.2 ± 2.46	55.5 ± 2.55	35.6 ± 2.74	28.8 ±1.01	0.99934
In	81.1 ± 2.10	68.5 ± 3.35	46.6 ± 2.19	28.0 ± 0.25	0.99923
Bi	51.0 ± 1.02	38.2 ± 2.63	27.9 ± 0.75	12.9 ± 0.50	0.99922
U	78.5 ± 2.74	65.5 ± 3.93	46.6 ± 3.21	27.4 ± 0.03	0.99923

Table 9. Metal concentrations from Mixture 2 in the aqueous phase (μg·L^{-1}); standard deviations (SD); correlation coefficients from calibration curves (R^2).

Analyte	Metal Concentrations ± Standard Deviations				Correlation Coefficients
	Blank no coffe waste μg/L	Sample 2a 100 mg coffe waste μg/L	Sample 2b 200 mg coffe waste μg/L	Sample 2c 300 mg coffe waste μg/L	
Pd	101.2 ± 0.40	27.7 ± 0.52	18.2 ± 0.02	16.4 ± 0.03	0.99992
Pt	102.3 ± 0.31	25.3 ± 0.18	12.4 ± 0.08	9.1 ± 0.08	0.99998
Sb	102.4 ± 0.20	55.0 ± 0.22	30.4 ± 0.12	26.0 ± 0.15	0.99999
Sn	42.4 ± 0.76	8.3 ± 0.17	6.6 ± 0.10	6.2 ± 0.03	0.99999
Ir	100.7 ± 0.10	93.0 ± 0.48	83.9 ± 0.16	76.1 ± 0.22	0.99998

The results show that the high removal efficiencies were obtained for some elements using 300 mg of adsorbent: Pt 91.1 %; Sn 85.4 %; Pd 83.8 %; Bi 74.7 %; Sb 74.6 %; and U 65.1 %. The maximum adsorption capacity was 0.0304 mg·g-1 for platinum. Palladium and uranium were also removed with satisfactory efficiency values of 83.8% and 65.1%, respectively. The efficiency for bismuth was 74.7 %. These results show that coffee waste with minimal processing may have application for decontamination and for recovery and reuse of elements from municipal wastewater or mining water.

Conclusions

Unpyrolyzed and pyrolyzed coffee waste were employed as inexpensive adsorbents for monuron and metals from aqueous solution. Monuron had a low adsorption on these materials compared to activated carbon. The coffee residue showed suitable adsorption for Bi, U, Pd, Pt, Sb, and Sn with potential application for wastewater treatment. The direct use of the material without treatment offers speed of preparation and low cost. This approach also recycles a waste product for further application. The results indicated that coffee grounds may be used as an inexpensive, and easily used adsorbent without treatment for the recovery of trace elements from aqueous solution.

Final Conclusions

Main purpose of this thesis was the determination and investigation of organic pollutants in surface water and wastewater and finding some efficient solutions to eliminate them from the environment. Considering the large number of contaminants and their diversity, that are constantly released into the environment, it requires the development of complex analytical methods in order to determine and quantify the correct behavior of these compounds. The issues of concern studied are: sorption of pollutants (biocides, triazines and phenylurea herbicides) into secondary sludge taken from a conventional wastewater treatment plants (WWTP), the influence of sodium azide on sorption, sludge-water distribution coefficients, quantification of analytes in the aqueous and solid phase, determination of linear alkylbenzene sulfonates (LASs) from water samples, the mass spectra of LASs, their elimination from WWTP on various amounts of zeolites, sorption of some organic pollutants (antioxidants, triazines, phenylurea herbicides, musk fragrances, antibacterial agents, antiepileptic drugs) on zeolites, development and application of low cost materials in wastewater treatment, characterization of materials, sorption of monuron and some trace metals.

For achieving this goals we used different methods and analytical tools: gas chromatography coupled with mass spectrometry (GC-MS), high performance liquid chromatography with mass spectrometry (HPLC-MS), inductively coupled plasma mass spectrometry (ICP-MS).

In sorption study onto activated sludge 41 micropollutants was investigated. For 27 contaminants, sludge-water distribution coefficients and their concentration dependency was determined for the first time. Both are major prerequisites for assessing their fate in WWTPs and thus their potential release into the environment via treated wastewater or via sludge amendment to agricultural land. Furthermore, the results of the present study imply important aspects for performing sorption experiments with fresh activated sludge. NaN_3 has been shown to be inappropriate for the deactivation of fresh sludge due to insufficient inhibition of microbial degradation and its influence on the sludge-water distribution. This is the first study confirming that increasing NaN_3 concentrations can lead to decreasing compound amounts sorbed to activated sludge. The Freundlich model was shown to be appropriate to describe the sorption behavior of various micropollutants in contact to secondary sludge.

In the second part of this thesis were determined a number of 20 compounds from linear alkylbenzene sulfonates (LASs) family and were carried out mass spectra of homologous series

C_{10}-, C_{11}-, C_{12}- and C_{13}-LAS as methyl esters derivatives. Furthemore, the molecular distribution of LAS isomers in water samples was described, from the profile of the characteristic ion chromatograms. The LASs compounds detected in WWTP contain chains with the number of carbon atom between 10 and 13, having concentration of: 47% (C_{10}-LAS), 40% (C_{11}-LAS), 11% (C_{12}-LAS) and 2% (C_{13}-LAS). It has been also studied, the rate of elimination of these compounds by sorption on zeolites. The average removal rate was 26.9 % (for 9 g/m^3) and 49.3 % (for 15 g/m^3). Besides linear alkylbenzene sulfonates (LASs) isomers removal from wastewater treatment plants, was also studied the removal efficiency of some organic pollutants from different classes of interest: antioxidants (BHA and BHT), triazines (Prometon, Atrazine, Propazine, Ametryn), phenylurea herbicides (Diuron, Isoproturon), musk fragrances (Galaxolide and Tonalide), antibacterial agent (Triclosan), antiepileptic drug (Carbamazepine). The best removal efficency are observed in the line with 15 g/m^3 zeolite added at the start of the bioreactor.

In the last part of this work was investigated the feasibility of using “low-cost” materials obtained from coffee residues: unpyrolyzed and pyrolyzed at 500 ºC coffee waste. These biosorbents have been used to eliminate one phenylurea derivative (monuron) and trace metals from aqueous solutions. To compare the efficency it was used as reference material activated carbon (a very good adsorbent). To the best of our knowledge, this is the first work on the adsorption of monuron using coffee waste as the adsorbent. For trace metals, in the literature, there are a large number of studies reporting adsorption on natural biosorbents. Adsorption studies on coffee waste materials are limited and were done either on a single component or a small number of metals. This study investigates the adsorption of a large number of metals (Ag, Bi, Co, Ga, In, Ni, U Pd, Pt, Sb, Sn şi Ir) in aqueous solution on different amounts of coffee residue with minimal processing (100 mg; 200 mg; 300 mg). Monuron had a low adsorption on these materials compared to activated carbon, yielding an elimination of 18.9% with unpyrolyzed coffee waste and 23.9% with pyrolyzed coffee waste. Instead, for trace metals, the coffee residue showed suitable adsorption with high removal efficiencies for some elements: Pt 91.1 %; Sn 85.4 %; Pd 83.8 %; Bi 74.7 %; Sb 74.6 %; and U 65.1 %, with real potential application for wastewater treatment. The results indicated that coffee grounds may be used as an inexpensive, and easily used adsorbent without treatment for the recovery of trace elements from aqueous solution.

Appendix 1

Publications

1. **Marincaş O**., Floare-Avram V., Feher I., Lazăr D., Voica C., Grosu I., 2016. Inexpensive adsorbents derived from coffee grounds for the treatment of wastewater. Anal. Lett. Article in Press. DOI: 10.1080/00032719.2015.1125913 **(IF: 1.031)**

2. Moldovan Z., Avram V., **Marincaş O**., Petrov P., Ternes T., 2011. The determination of the linear alkylbenzene sulfonate isomers in water samples by Gas-Chromatography/Mass Spectrometry. Journal of Chromatography A, Volume 1218, 343 – 349. **(IF: 4.531)**

3. Wick A., **Marincaş O**., Moldovan Z., Ternes T.A., 2011. Sorption of biocides, triazine and phenylurea herbicides, and UV-filters onto secondary sludge. Water Research, Volume 45, 3638 – 3652. **(IF: 4.865)**

4. **Marincaş O**., Petrov P., Ternes T., Avram V., Moldovan Z., 2009. The improvement of removal effects on organic pollutants in Wastewater Treatment Plants (WWTPs). Journal of Physics: Conference Series 182 (2009) 012040. **(IF: 0)**

Appendix 2

Scientific communications

10th International Conference „Processes in Isotopes and Molecules”, PIM 2015, 23 – 25 September 2015, Cluj – Napoca, Romania. „Low-cost adsorbent materials derived from coffee waste for wastewater decontamination”
Marincaş O., Floare-Avram V., Feher I., Lazăr D., Voica V., Grosu I.

10th International Conference „Processes in Isotopes and Molecules”, PIM 2015, 23 – 25 September 2015, Cluj – Napoca, Romania. „Assessment of river water quality using chemometric techniques”
Feher I., Voica C., Avram V., **Marincaş O**., Oprean I.

International Conference „Processes in Isotopes and Molecules”, PIM 2013, 25 – 27 September 2013, Cluj – Napoca, Romania. „Study of Flavour Compounds from Orange Juices by HS-SPME and GC-MS”
Schmutzer G., Feher I., **Marincaş O**., Avram V., Kovacs M.H., Măgdaş A., Covaciu F., David L., Moldovan Z.

International Conference „Processes in Isotopes and Molecules”, PIM 2013, 25 – 27 September 2013, Cluj – Napoca, Romania. „Characterization of some Romanian white whine by volatile compounds composition”
Avram V., Schmutzer G., **Marincaş O**., Hosu A., Cimpoiu C., Moldovan Z., Măruţoiu C.

9th GC x GC Symposium and 36th International Symposium on Capilary Chromatography, 27.05 – 01.06.2012, Riva del Garda, Italy. “Non-target pollutants detected in Prut River aqueous phase using GC/MS system”
Moldovan Z., Avram V., **Marincaş O**., Voica V., Tuşa F., Feher I., Schmutzer G., Kovacs M.H., Alder A.

14th International Symposium on Advance in Extraction Technologies (ExTech 2012), 24 – 26 September 2012, Messina, Italy. „Different methods used for sampling and extraction of micropollutants from water and sludge”
Marincaş O., Wick A., Moldovan Z., Alder A.C.

International Conference „Processes in Isotopes and Molecules”, PIM 2011, 29.09 – 01.10.2011, Cluj – Napoca, Romania. „The efficiency of different sampling methods for analysis of organic pollutants in surface waters”
Marincaş O., Moldovan Z., Avram V., Alder A.C.

International Conference „Processes in Isotopes and Molecules”, PIM 2011, 29.09 – 01.10.2011, Cluj – Napoca, Romania. „Determination of anionic surfactants in water samples using GC/MS system”
Moldovan Z., **Marincaş O**., Avram V., Schmutzer G.

International Conference „Processes in Isotopes and Molecules”, PIM 2011, 29.09 – 01.10.2011, Cluj – Napoca, Romania. „The use of Mass Spectrometry in the artwork studies”

Moldovan Z., Bratu I., Avram V., Schmutzer G., **Marincaş O**., Feher I., Mărutoiu C.

The 11th European Meeting on Environmental Chemistry, 8 – 11 December 2010, Portoroz, Slovenia. „Determination of organic pollutants in Prut River by GC/MS after concentration on a passive sampling device"
Moldovan Z., **Marincaş O**., Avram V., Alder A.C.

The XXXI-st Romanian Chemistry Conference, 6 – 8 October 2010, Ramnicu-Valcea, Romania. „Developement a passive sampling system for measurement of the organic contaminants in surface water"
Marincaş O., Moldovan Z., Alder A.C.

International Conference „Processes in Isotopes and Molecules", PIM 2009, 24 – 26 September 2009, Cluj – Napoca, Romania. "The improvement of removal effects on organic pollutants in Wastewater Treatment Plants (WWTP)"
Marincaş O., Petrov P., Ternes T., Avram V., Moldovan Z.

Workshop Water Framework Directive and Emerging Pollutants. Measures to minimize river contamination by WWTP discharges, 21– 22 April 2009, Federal Institute of Hydrology (BfG) Koblenz, Germany. "Characterization of water contaminants molecular distribution downstream of WWTP by GC/MS ion chromatograms"
Moldovan Z., Avram V., **Marincaş O**., Giurgiu M.

International Conference „Isotopic Processes", PIM 2008, 22 – 24 September 2008, Cluj – Napoca, Romania. „Aplication of stable isotope-labeled compounds for determination of the solid-water distribution coefficient (K_D) for organic pollutants in wastewater treatment plant"
Marincaş O., Wick A., Moldovan Z., Ternes T.

International Conference „Processes in Isotopes and Molecules", PIM 2007, 20– 22 September 2007, Cluj – Napoca, Romania. „Determination of pesticide residues in water samples using GC/MS system after SPE pre-concentration"
Moldovan Z., **Marincaş O**.

International Conference „EuroAnalysis XIV", 9 – 14 September 2007, Antwerp, Belgium. „Developement of a rapid method for the determination of polar herbicide residues in surface water samples using GC/IT – MS system after SPE pre – concentration"
Marincaş O., Moldovan Z.

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