Characteristics of wastewater from tunnel washing: case study from Brno

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ABSTRACT

The aim of this paper is present characteristics of tunnel wash water (TWW), varied management of European countries with the highest number of tunnels, characterization of contaminants and their origin and present results of a case study from Brno tunnel.

The case of study was located in the Brno tunnel, where TWW was pumped during spring and autumn washing and used for two sets of glasses filter pre-tests. The first set of glasses pre-tests required to determine the appropriate contact time, and the second set was focused on determining the amount of adsorbent. As adsorbents were used granulated activated carbon (GAC), food waste biochar, activated food waste biochar and wooden biochar. Analyses were focused on undissolved substances, C10-C40 hydrocarbons, chlorides, sulfates, heavy metals, and chemical elements. We conclude that filtration and adsorption on the filter medium, such as GAC or cheaper biochar, represents an eco-friendly way of treatment TWW, which belongs among the important strategies of circular economy.

1. Introduction

Road and highway tunnels, especially in densely urbanized areas, are polluted during car traffic. Polluted road surfaces, and tunnel equipment can negatively impact safety. Regulatory reports are created for each tunnel according to the tunnel length, traffic loading, and tunnel equipment settings. Among other, regulatory report specifies washing frequency and technological procedures. These processes generate tunnel wash water (TWW), which is usually highly polluted and potentially acutely toxic for aquatic organisms [1].

Depending on the traffic load and chosen washing method, the TWW contains a mix of organic and inorganic pollutants such as heavy metals (HMs), polyaromatic hydrocarbons (PAHs), chlorides, sulfates, microplastics, chemical elements such as Na, Ca, Mg, Zn and others. The frequency of washing processes ranges according to regulatory reports from 2 to 12 times per year and the volume of water ranges from 30 L to 150 L per linear meter of tunnel length [[2][3]. Washing is usually carried out by blasting surfaces with high pressurized water with or without added detergents. The amount of used detergents is usually in the range of 0.5-1% [4],[2],[3]. The water pressure ranges from 6 to 160 bars depending on the washing surface [2]. Regarding the measured values of pollutant concentrations contained in this TWW and lengths of road tunnels, is not negligible pollution.

In the CR, there are no statutory limits on the discharge of polluted TWW to recipient even though Act No. 254/2001 Coll. sets particularly hazardous and hazardous substances, which contain pollutants typically found in TWW. The most common methods of dealing with TWW are discharging into sewer system or directly into water recipient. In sewer system are often exceeded set limits according to the sewer regulations and these pollutants could negatively affected living organisms in downstream [1],[8].

In the near future, it could be expected that the legislation will be tightened from the point of view of monitored parameters in the TWW. This change in legislation will require the necessity to include an additional stage of TWW treatment, which could effectively and efficiently remove this pollution. It can be assumed to supplement the sedimentation technology with modern physical membrane technologies or to choose a more economical technological solution consisting in filtration and adsorption on the filter medium. granulated activated carbon (GAC) with a high S_{BET} has been successfully used as a filter medium to remove pollution from WW. An alternative and especially cheaper solution could be biochar, thus the solid carbon product after pyrolysis, and activated biochar with higher S_{BET}.

Treating TWW together with the aims of a circular economy (CE) strategy and the sustainability of raw products exploitation lead to search for an adequate/sustainable solution for the further usage of carbon waste and minimizing water pollution [13].

Current applied research of selected pollutants contained in the TWW is performed in laboratory conditions at AdMaS Research Centre, Brno University of Technology (BUT) in the CR. The samples of TWW were submitted to the Faculty of Chemistry, BUT for chemical analysis.

1.1. Management of TWW in EU

At present, the management of tunnel wash water varies from country to country. Of greatest concern in this respect is the fact that the countries with the highest number of tunnels do not consider treatment to be mandatory. Countries like Austria and Switzerland use sedimentation and filtration (e.g. mobile treatment trucks). However, countries like Norway, Sweden, and Italy use sedimentation for treatment albeit until now only in major tunnels close to cities [6].

The available data from Norway and Sweden state there are more than 1,000 tunnels and TWW is in most cases discharged untreated. However, in most of the bigger tunnels in and around cities, TWW is discharged into sedimentation basins inside or ponds outside the tunnel. In new tunnelling projects, a permit from the regional environmental authorities is needed to discharge TWW [5,6].

TWW in Switzerland and Austria is not allowed to be discharged untreated. In both countries, TWW is drained in a separate system and treated on site. In some cases, it is transported to an approved wastewater treatment plant (WTP) [6].

TWW is collected in a separate sedimentation basin. After sedimentation, the wash water is discharged into the public storm water system or treated on-site with a mobile TWW treatment unit. The mobile treatment unit consists of a sand or bag filter, flocculation and finally an activated carbon filter. The cleaned water is discharged into the surface water recipient, while the sediment is disposed of by a waste collector [6].

The Czech Republic has 29 road and highway tunnels with a total length of 43.5 km [6]. Italy has more than 1400 tunnels and in both of countries there is not mandatory to treat TWW. However, in new tunnels it is common practice to build a separate drainage system and collect TWW to sedimentation basins or WTP. In Brno TWW flows through street drains into the sedimentation tank and into sewer system or directly into water recipient.

1.2. Impact of TWW

In comparison with ordinary road runoff, studies showed that the pollutant concentrations in TWW are significantly higher at an otherwise similar level of traffic [5]. This is illustrated by data from Norway in Fig. 1.
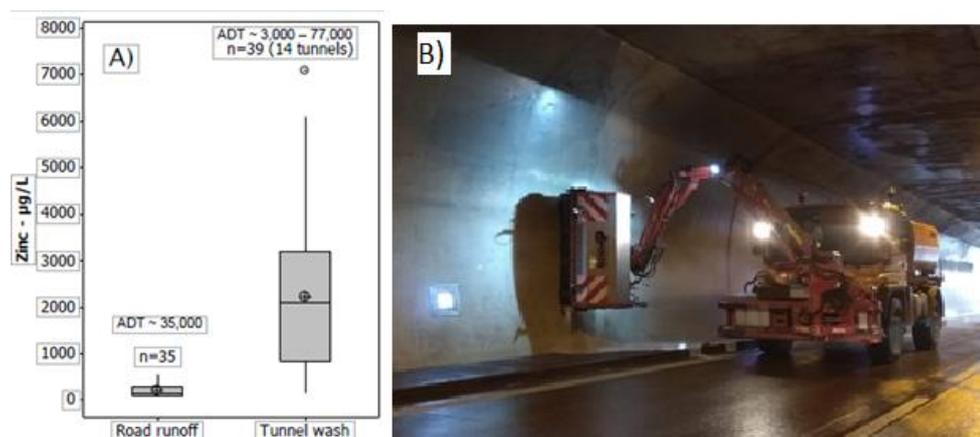

Fig. 1 A) Box-plot showing Zn concentrations in road runoff episodes (E6 Skullerud, based on 35 episodes) and TWW, tunnel wash sampling campaigns obtained from 14 tunnels [6]. Circle indicates an outlier and circles with cross indicate mean values. B) A washing event in Czech tunnel (photo: Ivo Korytář)

Fig. 2 represents a scheme of the temporal and spatial impacts of roads and tunnels [7]. During the washing processes large amounts of particles and pollutants are transported from the tunnel surface to the sewer system or aquatic environment, where may cause siltation of water bodies. The studies have shown that the pollutants may cause the physical alteration of habitats and have direct and indirect negative effects on organisms [8][1].
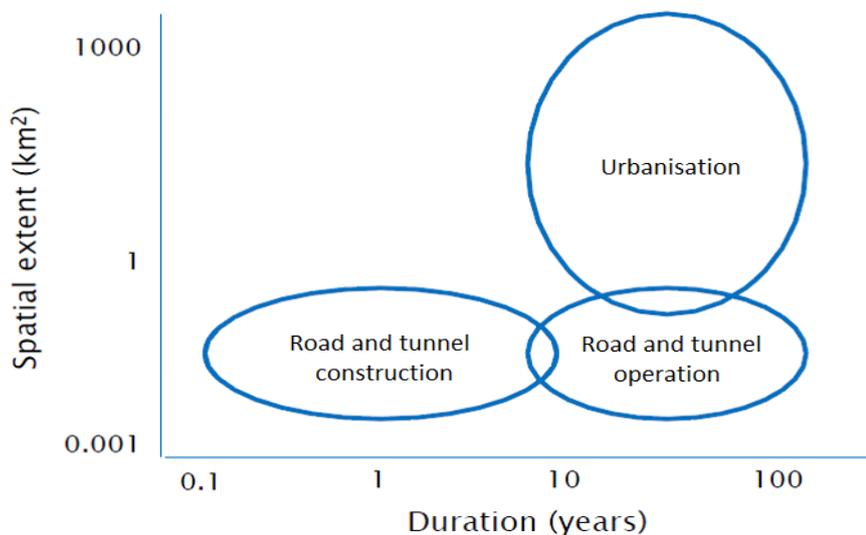
Fig. 2 The temporal and spatial extent of impacts caused by road and tunnel development. Construction occurs over relatively small time and space scales, while urbanisation occurs over much larger scales (axes are logarithmic). Modified from [7]

TWW typically contains a wide variety of chemical pollutants originating from vehicles, the road surface, technical infrastructure such as guardrails and traffic signs and during winter de-icing preparations. In addition, the release of chemical pollutants from accidental spillages may occur [5]. Common pollutants found in TWW are reported in Table 1.

Table 1 Pollutants found in TWW[5],[6]

Contaminant	Origin of pollution
Suspended solids	Weather-beaten surface material, tire
Pb	Tire, petroleum
AL	Tire, road surface (asphalt, bitumen)
Zn	Tire, oil drip, used lubricant oil
Fe	Breaks, vehicle body, road surface (asphalt, bitumen)
Cu	Brakes, fungicides
Cd	Tire, insecticides
Cr	Vehicle body, breaks
Ni	Oil and petroleum spill, metals, asphalt
Mn	Vehicle body, tire
Ti	Road surface (asphalt, bitumen)
Cl, cyanide, Na, Ca	Winter operating, de-icing
Hydrocarbons	Oil and petroleum spill, oil drip, used lubricant oil

Table 2Table describes the maximum and minimum measured values from selected studies and these are compared with the maximum values set by the sewer system for discharge of wastewater (WW) into the sewer system in the city of Brno.

Measured values that exceed the permitted limits are marked. According to the measured pH values, it is possible to determine that the TWW has an alkaline character. The maximum measured pH value of 11.77 exceeded the set limit for discharge into the sewage system. The suspended solids value exceeded the permitted values by almost ten times. The limits set by the regulatory report for discharges into sewers were further exceeded for chlorides, sulfates and phosphorus. The metals exceeded the limits for cadmium Cd, chromium Cr, copper Cu, nickel Ni, lead Pb and zinc Zn. These exceeded values correspond to Table , which lists the main indicators of substance pollution from automobile transport and compares it with limits from regulatory report [1],[3],[3],[9],[10],[11].

Table 2 The maximum and minimum measured values from selected studies and these are compared with the maximum values set by the sewer system for discharge of WW into the sewer system in the city of Brno, values that exceed the permitted limits are marked [1],[3],[3],[9],[11]

	Min	Max	Limits according to regulatory report of sewer system

			Mixed pattern	Scattering pattern
pH	7.00	**11.77**	6-9	
Turbidity (formazin nephelometric units)	8.77	2 706	-	-
SS [mg·L^{-1}]	13	**4 680**	400	600
TOC [mg·L^{-1}]	10.3	874	-	-
COD [mg·L^{-1}]	24	**2 691**	900	1 800
Chlorid Cl$^-$ [mg·L^{-1}]	260	**1 798**	200	300
Sulfat SO$_4$$^{2-}$ [mg·L^{-1}]	40.1	**275**	100	200
Phosphorus P [mg·L^{-1}]	1.9	**46.5**	7	15
Metals [µg·L^{-1}]				
As	<0.25	18	25	50
Ba	10	**553**	250	500
Ca	1200	234 000	250 000	500 000
Cd	0.1	**11**	2	4
Co	0.2	**43.4**	20	40
Cr	<2	**700**	50	100
Cu	7.5	**5 500**	1000	2 000
Fe	0.04	67 000	-	-
Hg	<0.001	0.001	50	100
Mg	< 500	286 000	150 000	300 000
Na	117 000	2 220 000	-	-
Ni	<1	**320**	50	100
Pb	0.05	**710**	80	100
Se	<5	**60**	10	20
Zn	9	**12 000**	1000	2000

According to the Table 2, it is obvious that the TWW has increased metal concentrations which some of them are categorized to particularly hazardous and hazardous substances [12]. Because of using of road salt, increased concentrations of sodium and associated chloride occur. Discharging into the recipient, studies point to the risk of negative effects on organisms living in the recipient.

2. Material and methods

The adsorbing efficiency is tested for biochar, which was produced by medium-temperature pyrolysis from food waste and wooden biochar. The efficiency of biochar adsorbing was compared to a conventional absorbent - GAC. For experiments was used TWW from the road tunnel in Brno.

2.1. Washing of road tunnels

The washing of Brno, road tunnels under the administration of the Directorate of Roads and Motorways of the Czech Republic takes place twice a year, always in spring and autumn. Washing with pressurized potable water with added detergent is used to clean the road, sidewalk, ceiling, and tunnel equipment. The combination of mechanical brush washing, and pressurized water is only used for washing the tunnel lining. In Brno TWW flows through street drains into the sedimentation tank and into sewer system or directly into water recipient. Approximately 600 L of TWW for testing purposes was pumped from sedimentation tank into the prepared Intermediate bulk containers (IBC) tank.

The total length of road tunnels in Brno is 4.991 m and the total water consumption during one washing is 790 m3. The average water consumption is 158.3 L per linear metre of tunnel, including the ceiling, tunnel lining, sidewalk, road, and all equipment.

2.2. Adsorption

Adsorption is a phenomenon in which adsorbate from the liquid or gas phase are attracted to the surface of the solid adsorbent. The adsorbate accumulates on a specific surface of the adsorbent and after adsorption, the concentration of adsorbate on the surface of the adsorbent is many times greater than in the environment from which the substance is adsorbed [14].

The basic characteristics of adsorbent are granularity, porosity, specific surface area, and chemical properties [14].

For powdered adsorbent dosing into contact tanks with a high degree of agitation, the most common limiting step is the pore diffusion rate, on the other hand, in continuous flow systems using dynamic adsorption, where the medium passes through the adsorbent layer, is usually a limiting process the rate of diffusion to the surface of particle [14].

Fig. 3 represents a scheme of the association of molecular mass growth mechanisms and mobilization processes.
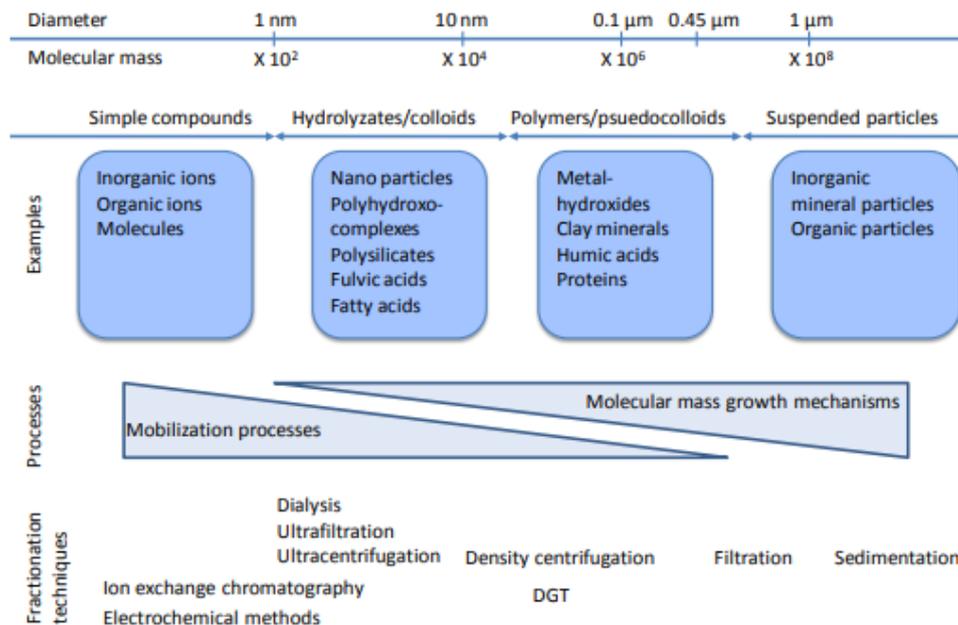

Fig. 3 Association of metal and metalloid species with compounds in different size ranges. Molecular mass growth mechanisms include hydrolysis, complexation, polymerization, colloid formation and aggregation. Mobilisations mechanisms include desorption, dissolution and dispersion [5].

2.3. Biochar

Biochar is a carbonaceous material obtained from thermochemical conversion of biomass without oxygen access, the so-called microwave pyrolysis, or weak pyrolysis - torrefaction. The biochar properties are strictly dependent on the composition of the original processed organic substance and the technology of applied pyrolysis (especially temperature). Generally, biochar is characterized by a high specific surface, porous structure, high calorific value and abundant representation of functional groups and mineral constituents allowing adsorption [15]5,[15]6,[17]7,[18].

The different characteristics of the biochar depend on the type of organic material being processed and the processing technology. Specific properties of biochar, such as surface area, pore size and cation exchange capacity (CEC), affect the ability of biochar to adsorb water and retain nutrients [18].

2.4. Determination of pH, EC, DTS and S_{BET} specific surface area

Electric conductivity (EC), pH and total dissolved solids (DTS) was measured on multi-parameter meter (inoLab® Multi 9420 IDS, WTW), and calibration was performed on pH 7 buffer.

The specific surface area (S_{BET}) of the adsorbents ($g \cdot m^{-2}$) as a fundamental indicator is measured by the BET method (Brunauer, Emmett, Teller). This method uses gas adsorption with the following characteristics of the analysis process:

- analytical gas: nitrogen;
- pressure adsorption/desorption tolerance: 0.050/0.050;
- adsorption/desorption equilibrium time: 240/240 s;
- equilibrium time adsorption / desorption output: 480/480 s;
- temperature: -195.8 °C.

For specific surface analysis, five points were measured and assessed using the multi-point BET method on a Quantachrome Nova 3200e. All samples were degassed in a vacuum oven for 24 hours at 150 °C.

2.5. Preparing of activated biochar

The specific surface area of the food waste biochar (FWB) was increased by activating, with concentrated hydrochloric acid HCl. Prior to the activation, the biochar pellets were crushed and sieved to the required fraction

of 0.5 – 2 mm. This fraction was chosen according to set of sieves, that were the closest to the used GAC, which is supplied in a fraction of 0.42-1.7 mm. The total amount of FWB determin to activation was 45 g. Upon activation, the entire surface of the biochar was in contact with concentrated HCl for 24 hours. After the contact time (CT) has elapsed, it was necessary to remove demineralized substances and all HCl from the porous structure of the biochar. To a beaker was added 200 ml of demineralized water and 5.0 g of activated biochar. The samples were placed in a thermostat cabinet and stirred at a constant temperature of 40 °C for 24 hours. The biochar samples were then filtered through filter paper and placed in a hot air oven. Samples of the activated biochar were dried at 80°C for 24 hours.

2.6. Sample preparation

TWW was sampled during spring and autumn tunnel washing 2020. To determine CT and concentration of adsorbents were pre-tests divided to two sets of pre-tests. For the first set of glasses pre-test was used spring TWW and autumn TWW for second set. The tested samples were poured into dark, half-litre bottles and an adsorbent was added. For chemical analysis of one sample was needed 2 L of TWW.

The first set of glasses pre-tests required to determine the appropriate CT. Tested CTs were 0-7-24-46 h and concentrations of adsorbents were for all samples the same 2.5 $g \cdot L^{-1}$. The samples were placed in thermostat cabinets and stirred at a constant temperature of 23.0-25.0 °C.

The second set of glasses pre-tests was focused on determining the amount of adsorbent. For maximal homogenization of the sample, 10.0 L of TWW was taken from the IBC tank into a smaller canister. Before each pour of the tested sample, the 10.0 L canister was stirred for 30 s. The amount of adsorbent for pre-tests was determined as 1.0 $mg \cdot L^{-1}$, 2.5 $mg \cdot L^{-1}$ and 4.0 $mg \cdot L^{-1}$. The samples were placed in thermostat cabinets and stirred at a constant temperature of 20.5-23.0 °C for 1 hour.

After the specified CT of TWW with the selected adsorbent, the samples were filtered through filter paper and the values of pH [-], temperature [°C], redox potential U [mV], salinity [-], conductivity [$\mu S \cdot cm^{-1}$] and specific resistance [$\Omega \cdot cm$] were measured.

These samples were submitted to the Faculty of Chemistry, BUT for chemical analysis. Analyses were monitored the following pollutants: undissolved substances (US), C10-C40 hydrocarbons, chlorides, sulfates, HMs, chemical elements such as Na, Ca, Mg, and others.

2.7. Determination

Determination of Cd, Cu, Ni, Pb, Cr, and As

For the determination of HMs contents were performed using atomic absorption spectrometer with electrothermal atomization with a continuous radiation source ContrAA 800 from Analytik Jena. Optimal measurement parameters and specific temperature program were used for each HM. Injected volume were 20 μl. All obtained results are the average of three separate independent determinations, each was measured for atomic absorption spectrometer three times.

Table 3 Thermal programs for the determination of selected HMs: As, Cd, Cr, Cu, Pb, and Ni

HMs	Wavelength [nm]	Modificator	Drying 1/2/3 [°C]	Pyrolysis [°C]	Atomization [°C]	Cleaning [°C]
Cd	228.8018	$Pd/Mg(NO_3)_2$	80, 90, 110	350, 700	1600	2450
Cu	324.754	$Pd/Mg(NO_3)_2$	80, 90, 110	350, 1100	2000	2450
Ni	232.003	$Mg(NO_3)_2$	80, 90, 110	350, 1100	2200	2450
Pb	283.306	$Pd/Mg(NO_3)_2$	80, 90, 110	350, 900	1500	2450
Cr	357.8687	$Mg(NO_3)_2$	80, 90, 110	350, 1300	2300	2450
As	193.696	$Pd/Mg(NO_3)_2$	80, 90, 110	350, 1100	2200	2450

Determination of Zn, Fe, Mg, Na, Ca and Hg

For the determination of Zn, Fe and Mg contents were used the same atomic absorption spectrometer as for HMs with atomization by flame. Optimal measurement parameters are described in Table .

Table 4 Optimal measurement parameters for determination of Zn, Fe and Mg

Element	Wavelength [nm]	Acetylene-air flow [$l \cdot h^{-1}$]	Burner height [mm]
Fe	248.327	60	6
Mg	285.2125	70	6
Zn	213.857	50	6

Na and Ca were measured using a PFP7 single channel flame photometer with wavelength of 589 and 423 nm.

Hg was measured using an Advanced Mercury Analyzer AMA 254 using a wavelength of 253.65 nm. During the measurement, drying was performed at 120 °C for 60 s, then combustion in an oxygen atmosphere at 650 °C for 60 s and finally cleaning of the system for 45 s. The sample volume was 100 μl.

All samples were measured 3 times and the resulting average values were evaluated from the measured calibration curve for individual elements.

Table 5 Determined LOD and LOQ for measured elements

Element	LOD [μg·L⁻¹]	LOQ [μg·L⁻¹]	Element	LOD [μg·L⁻¹]	LOQ [μg·L⁻¹]
Hg	0.774	2.579	Ni	2.169	6.5
Cu	0.29	0.875	Mg	1.578	4.7
Zn	1.578	4.7	Fe	5.024	16.748
As	3.756	11.27	Na	200	-
Cr	0.9853	2.956	Ca	15000	-
Pb	2.385	9.69			

Notes: LOD-limit of detection, LOQ-limit of qualification

Determination of C10 - C40 hydrocarbons
Parameters C10-C40 are expressed as the total sum of the integrated signal, which is defined by the retention time of decane and tetracontane. The method was used for the analysis of TWW with a limit of determination of 0.2 mg·L⁻¹.

The measurement was performed on an Agilent 5890 gas chromatograph with a flame ionization detector (GC/FID). The injection was split 1:20. To 800 ml of the TWW sample was added 10 ml of n-heptane (n-decane and tetracontane 10 mg·L⁻¹). The sample was shaken on a shaker for 1 hour. After phase separation, the organic phase was collected and dried on a silica gel and sodium sulfate column. About 1 ml was taken from the thus dried sample for GC/FID analysis. Hydrogen (2 ml·min⁻¹) was used as the carrier gas, the temperature program was 50 °C for 5 min, then 30 °C·min⁻¹ to 320 °C, 320 °C for 15 min. For calibration was used mineral oil in n-heptane in concentrations of 0.2-400 mg·L⁻¹.

3. Results and discussion

The glasses pre-tests required to determine the concentrations of adsorbents as well as the appropriate CT. The results included these parameters: US, HMs, C10-C40, chlorides, sulfates, chemical elements such as Na, Ca, Mg, Zn and others.

3.1. Glasses pre-tests – CT
TWW composition from spring washing and after adsorption is reported in Table 1. Three adsorbents were used: GAC, food waste biochar (FWB), and activated food waste biochar (AFWB). Concentrations of adsorbents were for all samples the same 2.5 g·L⁻¹. Tested CTs were 0-7-24-46 hours. These selected parameters were measured: pH, temperature, ORP, salinity, EC, TDS, spec. ρ, C10-C40, and chlorides. All samples were filtered through the filter paper before analyses.

Table 6 TWW composition from spring washing and after adsorption: EC, TDS, spec. ρ, C10-C40, and chlorides

Adsorbent	Time [h]	Weight [g·L⁻¹]	pH -	Temperature [°C]	ORP [mV]	Salinity	EC [μS·cm⁻¹]	TDS [mg·L⁻¹]	spec. ρ [Ω·cm]	C10-C40 [mg·L⁻¹]	Chlorides [mg·L⁻¹]
GAC	0	0	7.961	26.8	168.4	0.9	1837	1837	544	15.65	-
	7	2.5	8.574	25.3	139.0	0.9	1870	1869	535	15.75	-
	24	2.5	8.791	24.9	97.2	0.9	1869	1869	535	14.65	-
	46	2.5	8.883	24.6	165.0	0.9	1880	1880	532	8.17	-
FWB	0	0	7.906	17.8	198.5	0.9	1801	1801	555	5.08	4100
	7	2.5	8.778	19.1	160.5	1.1	2180	2180	459	4.52	4100
	24	2.5	8.815	23.2	167.9	1.1	2240	2240	446	6.79	4150
	46	2.5	8.918	23.3	168.0	1.1	2200	2200	455	4.54	4600
AFWB	0	0	7.906	17.8	198.5	0.9	1801	1801	555	5.08	4100
	7	2.5	8.366	19.8	197.7	0.9	1855	1855	539	4.20	4850

| 25 | 2.5 | 8.604 | 24.9 | 193.5 | 0.9 | 1850 | 1850 | 540 | 4.90 | 4050 |
| 46 | 2.5 | 8.680 | 24.9 | 166.1 | 0.9 | 1880 | 1880 | 532 | 4.71 | 3850 |

Notes: GAC-granular activated carbon, FWB-food waste biochar, AFWB-activated food waste biochar, ORP-oxidation/reduction potential, TDS-total dissolved solids, Spec. ρ-specific electrical resistance, EC-electrical conductivity, the values of chlorides after adsorption with GAC were lost

According to Table 6, the pH of TWW was represented ranging from 7.906-7.961 and after adsorption the pH was higher ranging from 8.366-8.918.

The temperature of TWW depended on outside weather and the CT with adsorbent. The IBC tank with spring TWW was stocked outside, autumn TWW was stocked inside because of constant temperature and conditionals. The temperature of TWW was 17.8-26.8 °C and after adsorption in thermostat cabinets the temperature was 19.1-25.3 °C.

TWW had ORP 168.4-198.5 mV, after adsorption with GAC was ORP lower 139.0-97.2 mV until CT was 46 hours, than was ORP 165.0 mV. Similar situation was after adsorption with FWB, ORP was lower after CT 7 hours, and after longer CT the ORP was 167.9-168.0 mV. TWW with AFWB had ORP 198.5-166.1 mV.

TWW with GAC and AFWB had for whole time the same value of salinity 0.9. After adsorption with FWB salinity increased to value 1.1.

TWW had EC and TDS 1801-1837 µS·cm^{-1}, the EC and TDS after adsorption with GAC was higher 1869-1888 µS·cm^{-1}. The increase of EC and TDS was higher after adsorption with FWB than with GAC 2180-2240 µS·cm^{-1}. The values of EC and TDS after adsorption with AFWB were similar with GAC values 1850-1880 µS·cm^{-1}.

TWW had spec. ρ 544-555 Ω·cm, after adsorption with GAC and AFWB the values of spec. ρ were similar 532-540 Ω·cm. Spec. ρ after adsorption with FWB was lower 446-459 Ω·cm.

TWW had C10-C40 15.65 mg·L^{-1}, after adsorption with GAC the values of C10-C40 were lower 8.17-15.75 mg·L^{-1}. The C10-C40 before adsorption was 5.08 mg·L^{-1}, after adsorption with FWB was 4.52-6.79 mg·L^{-1}, and after adsorption with AFWB was 4.2-4.9 mg·L^{-1}.

TWW had 4100 mg·L^{-1} chlorides, after adsorption with FWB were chlorides higher 4100-4600 mg·L^{-1}, and after adsorption with AFWB was 3850-4850 mg·L^{-1}.

TWW composition from spring washing and after adsorption is reported in Table 7. Three adsorbents were used: GAC, FWB, AFWB. Concentrations of adsorbents were for all samples the same 2.5 g·L^{-1}. Tested CTs were 0-7-24-46 hours. These selected parameters were measured: Cu, Pb, Ni, Cr, As, Cd, Zn, Na, Ca, Mg, Fe, and Hg. All samples were filtered through the filter paper before analyses.

Table 7 TWW composition from spring washing and after adsorption: Cu, Ni, Cr, As, Zn, Na, Ca, Mg

Adsorbent Time	Weight	Cu	Ni	Cr	As	Zn	Na	Ca	Mg
[h]	[g·L^{-1}]	[µg·L^{-1}]	[µg·L^{-1}]	[µg·L^{-1}]	[µg·L^{-1}]	[µg·L^{-1}]	[mg·L^{-1}]	[mg·L^{-1}]	[mg·L^{-1}]
GAC 0	0	4.45 ± 0.07	35.25 ± 1.05	0.98 ± 0.05	5.76 ± 1.08	21.36 ± 0.65	293.33 ± 5.77	67.00 ± 0.00	6.78 ± 0.04
7	2.5	8.97 ± 0.49	34.85 ± 0.39	<LOD	<LOD	10.97 ± 0.32	253.33 ± 5.77	61.67 ± 0.58	8.79 ± 0.17
24	2.5	4.01 ± 0.03	36.73 ± 0.15	<LOD	<LOD	4.10 ± 0.28	270.00 ± 0.00	54.67 ± 0.58	11.24 ± 0.06
46	2.5	3.98 ± 0.25	32.53 ± 0.05	<LOD	<LOD	9.32 ± 0.34	260.00 ± 0.00	55.33 ± 0.58	10.45 ± 0.13
FWB 0	0	8.99 ± 0.18	39.85 ± 0.39	<LOD	<LOD	141.82 ± 1.53	270.00 ± 0.00	56.00 ± 0.00	7.77 ± 0.18
7	2.5	7.05 ± 0.29	40.10 ± 1.05	<LOD	<LOD	8.55 ± 0.39	310.00 ± 0.00	69.67 ± 0.58	7.91 ± 0.19
24	2.5	3.44 ± 0.30	38.86 ± 0.13	<LOD	<LOD	11.95 ± 0.46	333.33 ± 5.77	70.00 ± 0.00	9.94 ± 0.22
46	2.5	7.75 ± 0.04	35.10 ± 0.21	<LOD	<LOD	13.06 ± 0.11	366.67 ± 5.77	68.00 ± 0.00	9.54 ± 0.23
AFWB 0	0	8.99 ± 0.18	39.85 ± 0.39	<LOD	<LOD	141.82 ± 1.53	270.00 ± 0.00	56.00 ± 0.00	7.77 ± 0.18
7	2.5	6.14 ± 0.22	33.47 ± 0.01	<LOD	<LOD	27.57 ± 0.65	280.00 ± 0.00	63.00 ± 0.00	8.64 ± 0.13
25	2.5	2.65 ± 0.10	35.25 ± 0.08	<LOD	<LOD	16.76 ± 0.44	280.00 ± 0.00	62.00 ± 0.00	9.44 ± 0.30
46	2.5	5.03 ± 0.24	36.39 ± 0.30	<LOD	<LOD	25.11 ± 0.34	286.67 ± 5.77	67.00 ± 0.00	9.11 ± 0.21

Notes: GAC-granular activated carbon, FWB-food waste biochar, AFWB-activated food waste biochar, LOD-limit of detection, LOQ-limit of qualification

According to Table 7, TWW before adsorption had Cu 4.45 µg·L^{-1}, after adsorption with GAC was Cu 3.98-8.97 µg·L^{-1}. Ni was 35.25 µg·L^{-1} before adsorption and 32.53-36.73 µg·L^{-1} after adsorption. Cr was 0.98 µg·L^{-1} before adsorption and after adsorption was not detected. As was 5.76 µg·L^{-1} before adsorption and after adsorption was

not detected. Zn was 21.36 µg·L^{-1} before adsorption and 4.1-10.97 µg·L^{-1} after adsorption. Na was 293.33 mg·L^{-1} before adsorption, after adsorption were values lower 253.33-270.0 mg·L^{-1}. Ca was 67.0 mg·L^{-1} before adsorption, after adsorption were values lower 54.67-61.67 mg·L^{-1}. Mg was 6.78 mg·L^{-1} before adsorption and 8.79-11.24 mg·L^{-1} after adsorption. Values of Pb, Cd, Fe, Hg were in TWW under limit of detection.

TWW before adsorption had Cu 8.99 µg·L^{-1}, after adsorption with FWB were values lower 3.44-7.75 µg·L^{-1}. Ni was 39.85 µg·L^{-1} before adsorption and 35.1-40.1 µg·L^{-1} after adsorption. Zn was 141.82 µg·L^{-1} before adsorption, after adsorption were values lower 8.55-13.06 µg·L^{-1}. Na was 270 mg·L^{-1} before adsorption and 310.0-366.67 mg·L^{-1} after adsorption. Ca was 56.0 mg·L^{-1} before adsorption and 28.0-70.0 mg·L^{-1} after adsorption. Mg was 7.77 mg·L^{-1} before adsorption and 7.91-9.94 mg·L^{-1} after adsorption. Values of Cr, As, Pb, Cd, Fe, Hg were in TWW under limit of detection.

TWW before adsorption had Cu 8.99 µg·L^{-1}, after adsorption with AFWB were values lower 2.65-6.14 µg·L^{-1}. Ni was 39.85 µg·L^{-1} before adsorption, after adsorption were values lower 33.47-36.39 µg·L^{-1}. Zn was 141.82 µg·L^{-1} before adsorption, after adsorption were values lower 16.76-27.57 µg·L^{-1}. Na was 270 mg·L^{-1} before adsorption and 280.0-286.67 mg·L^{-1} after adsorption. Ca was 56.0 mg·L^{-1} before adsorption and 62.0-67.0mg·L^{-1} after adsorption. Mg was 7.77 mg·L^{-1} before adsorption and 8.64-9.44 mg·L^{-1} after adsorption. Values of Cr, As, Pb, Cd, Fe, Hg were in TWW under limit of detection.

3.2. Glasses pre-tests – adsorbent concentration

TWW composition from autumn washing and after adsorption is reported in Table 8. Three adsorbents were used: wooden biochar (WB), AFWB, and GAC. Tested concentrations of adsorbents were 1.0 g·L^{-1}, 2.5 g·L^{-1}, 4.0 g·L^{-1}. CTs were for all samples the same 1 hour. These selected parameters were measured: pH, temperature, ORP, Salinity, EC, TDS, and spec. ρ. All samples were filtered through the filter paper before analyses.

Table 8 TWW composition from autumn washing and after adsorption: EC, TDS, spec. ρ, C10-C40

Adsorbent	Weight [g·L^{-1}]	pH -	Temperature [°C]	ORP [mV]	Salinity	EC [µS·cm^{-1}]	TDS [mg·L^{-1}]	Spec. ρ [Ω·cm]
WB	0.0	8.397	21.9	-63.4	0.5	1084	1084	922
	1.0	8.435	22.1	-65.5	0.5	1090	1090	917
	2.5	8.522	22.2	-70.4	0.5	1109	1109	903
	4.0	8.574	22.2	-73.3	0.5	1089	1089	918
AFWB	0.0	8.395	21.1	-63.2	0.5	1090	1090	916
	1.0	8.398	22.5	-63.5	0.5	1093	1093	915
	2.5	8.306	22.4	-58.6	0.5	1087	1087	920
	4.0	8.274	22.5	-57.0	0.5	1100	1100	909
GAC	0.0	8.288	21.5	-57.4	0.5	1085	1085	922
	1.0	8.421	21.8	-64.8	0.5	1094	1094	914
	2.5	8.546	21.9	-71.6	0.5	1108	1108	903
	4.0	8.658	21.9	-77.7	0.5	1136	1136	881

Notes: WB-wooden biochar, AFWB-activated food waste biochar, GAC-granular activated carbon, ORP-oxidation/reduction potential, TDS-total dissolved solids, Spec. ρ-specific electrical resistance, EC-electrical conductivity

According to Table 8, the pH of TWW was represented ranging from 8.288-8.397 and after adsorption the pH ranging from 8.274-8.658.

The temperature of TWW was ranging from 21.1-22.5 °C.

TWW had ORP form -57.4 mV to -63.4 mV, after adsorption with GAC and WB was ORP lower from -64.8 mV to –77.7 mV. TWW after adsorption with AFWB was ORP from -63.5 mV to -57.0 mV.

TWW with and without adsorbent had for whole time the same value of salinity 0.5.

TWW had EC and TDS 1084-1090 µS·cm^{-1}, the EC and TDS after adsorption with WB was higher 1089-1109 µS·cm^{-1}. After adsorption with AFWB were EC and TDS 1087-1100 µS·cm^{-1}. The values of EC and TDS after adsorption with GAC were 1094-1136 µS·cm^{-1}.

TWW had spec. ρ 916-922 Ω·cm, after adsorption with WB and AFWB the values of spec. ρ were similar 903-920 Ω·cm. Spec. ρ after adsorption with GAC was lower 881-914 Ω·cm.

TWW composition from autumn washing and after adsorption is reported in Table 92. Three adsorbents were used: WB, AFWB, and GAC. Tested concentrations of adsorbents were 1.0 g·L^{-1}, 2.5 g·L^{-1}, 4.0 g·L^{-1}. CTs were

for all samples the same 1 hour. These selected parameters were measured: pH, US, tenside, C10-C40, chlorides, and sulfates. The samples with (UF) were analysed unfiltered, the rest of all samples were filtered through the filter paper before analyses. The sample without adsorbent was analysed immediately after tunnel washing, the rest of samples were analysed after 5 months cause of absence of adsorbents.

Table 93 TWW composition from autumn washing and after adsorption: pH, US, tenside, C10-C40, chlorides, and sulfates

Adsorbent	Weight [g·L^{-1}]	pH -	US [g·L^{-1}]	Tenside [mg·L^{-1}]	C10-C40 [g·L^{-1}]	Chlorides [mg·L^{-1}]	Sulfates [mg·L^{-1}]
-	0.0		0.62 (UF)	0.44	0.02 (UF)	4400.00	71.00
WB	0.0	8.397	0.45 (UF)	0.14	0.13 (UF)	220.00	62.00
	1.0	8.435	-	0.18	0.01	185.00	55.00
	2.5	8.522	-	0.16	0.02	155.00	56.00
	4.0	8.574	-	0.22	0.17	145.00	66.00
AFWB	0.0	8.395	0.42 (UF)	0.31	0.64 (UF)	185.00	73.00
	1.0	8.398	-	0.36	0.17	150.00	64.00
	2.5	8.306	-	0.17	0.22	170.00	79.00
	4.0	8.274	-	0.16	0.15	185.00	83.00
GAC	0.0	8.288	0.16 (UF)	0.25	0.05 (UF)	225.00	63.00
	1.0	8.421	-	0.27	0.11	190.00	84.00
	2.5	8.546	-	0.24	0.26	180.00	80.00
	4.0	8.658	-	0.26	0.32	210.00	78.00

Notes: US-undissolved substances, WB-wooden biochar, AFWB-activated food waste biochar, GAC-granular activated carbon, UF-unfiltered samples, F-filtered samples

TWW analysed immediately after tunnel washing, and according to Table 9 had value of US 0.62 g·L^{-1}, tenside 0.44 mg·L^{-1}, C10-C40 0.02 g·L^{-1}, chlorides 4400.0 mg·L^{-1}, and sulfates 71.0 mg·L^{-1}. The values of US and C10-C40 were measured unfiltered.

TWW before adsorption had US 0.16-0.45 g·L^{-1}, after adsorption was not US detected. It was due to filtration through the filter paper.

TWW before adsorption had tenside 0.14 mg·L^{-1}, after adsorption with WB was tenside 0.16-0.22 mg·L^{-1}. C10-C40 were 0.13 g·L^{-1} before adsorption and 0.01-0.17 g·L^{-1} after adsorption. Chlorides were 220.0 mg·L^{-1} before adsorption. after adsorption were values lower 145.0-185.0 mg·L^{-1}. Sulfates were 62.0 mg·L^{-1} before adsorption and 55.0-66.0 mg·L^{-1} after adsorption.

TWW before adsorption had tenside 0.31 mg·L^{-1}, after adsorption with AFWB was tenside 0.16-0.36 mg·L^{-1}. C10-C40 were 0.64 g·L^{-1} before adsorption, after adsorption were values lower 0.15-0.22 g·L^{-1}. Chlorides were 185.0 mg·L^{-1} before adsorption and 150.0-185.0 mg·L^{-1} after adsorption. Sulfates were 73.0 mg·L^{-1} before adsorption and 64.0-83.0 mg·L^{-1} after adsorption.

TWW before adsorption had tenside 0.25 mg·L^{-1}, after adsorption with GAC was tenside 0.24-0.27 mg·L^{-1}. C10-C40 were 0.05 g·L^{-1} before adsorption and 0.11-0.32 g·L^{-1} after adsorption. Chlorides were 225.0 mg·L^{-1} before adsorption, after adsorption were values lower 180.0-210.0 mg·L^{-1}. Sulfates were 63.0 mg·L^{-1} before adsorption and 78.0-84.0 mg·L^{-1} after adsorption.

TWW composition from autumn washing and after adsorption is reported in Table 40. Three adsorbents were used: WB, AFWB, and GAC. Tested concentrations of adsorbents were 1.0 g·L^{-1}, 2.5 g·L^{-1}, 4.0 g·L^{-1}. Tested CTs were for all samples the same 1 hour. These selected parameters were measured: Cu, Pb, Ni, Cr, As, Cd, Zn, Na, Ca, Mg, Fe, and Hg. All samples were filtered through the filter paper before analyses.

Table 10 TWW composition from autumn washing and after adsorption: Cu, Ni, Cr, Zn, Na, Ca, Mg, Fe

Adsorbent	Weight [g·L^{-1}]	Cu [µg·L^{-1}]	Ni [µg·L^{-1}]	Cr [µg·L^{-1}]	Zn [µg·L^{-1}]	Na [mg·L^{-1}]	Ca [mg·L^{-1}]	Mg [mg·L^{-1}]	Fe [µg·L^{-1}]
-	0.00	29.16 ± 0.23	42.17 ± 3.00	3.16 ± 0.09	139.98 ± 3.87	130.00 ± 0.00	79.33 ± 0.58	11.12 ± 0.27	311.44 ± 9.16
WB	0.0	1.78 ± 0.15	<LOD	<LOD	48.27 ± 4.96	113.33 ± 5.77	57.33 ± 2.08	8.81 ± 0.19	254.36 ± 8.71
	1.0	<LOQ	<LOD	<LOD	8.77 ± 0.18	186.67 ± 5.77	58.67 ± 0.58	9.26 ± 0.18	<LOD
	2.5	2.39 ± 0.12	<LOD	<LOD	29.49 ± 1.13	186.67 ± 5.77	57.33 ± 1.53	10.32 ± 0.14	<LOD

	4.0	2.07 ± 0.07	<LOD	<LOD	17.89 ± 0.14	96.67 ± 5.77	57.67 ± 1.15	10.95 ± 0.25	<LOD
AFWB	0.0	1.51 ± 0.11	<LOD	<LOD	29.59 ± 5.10	66.67 ± 5.77	60.33 ± 1.15	9.31 ± 0.25	130.84 ± 12.98
	1.0	<LOQ	<LOD	<LOD	9.29 ± 0.37	110.00 ± 0.00	59.00 ± 1.00	9.06 ± 0.20	<LOD
	2.5	1.08 ± 0.22	<LOD	<LOD	9.66 ± 0.25	76.67 ± 5.77	60.00 ± 1.73	8.55 ± 0.09	<LOD
	4.0	1.57 ± 0.12	<LOD	<LOD	21.14 ± 0.95	96.67 ± 5.77	63.00 ± 0.00	9.18 ± 0.20	<LOD
GAC	0.0	1.38 ± 0.42	<LOD	<LOD	29.50 ± 1.46	100.00 ± 10.00	58.00 ± 1.00	8.80 ± 0.14	234.12 ± 5.89
	1.0	0.92 ± 0.03	<LOD	<LOD	<LOD	123.33 ± 5.77	54.00 ± 0.00	9.30 ± 0.19	<LOD
	2.5	0.93 ± 0.05	<LOD	<LOD	<LOD	60.00 ± 0.00	53.67 ± 0.58	9.08 ± 0.22	<LOD
	4.0	1.17 ± 0.00	<LOD	<LOD	<LOD	116.67 ± 15.28	52.67 ± 1.53	9.48 ± 0.25	<LOD

Notes: WB-wooden biochar, AFWB-activated food waste biochar, GAC-granular activated carbon, LOD-limit of detection, LOQ-limit of qualification

TWW analysed immediately after tunnel washing had value of Cu 29.16 µg·L^{-1}, Ni 42.17 µg·L^{-1}, Cr 3.16 µg·L^{-1}, Zn 139.98 µg·L^{-1}, Na 130.0 mg·L^{-1}, Ca 79.33 mg·L^{-1}, Mg 11.12 mg·L^{-1}, and Fe 311.44 µg·L^{-1}. Pb, As, Cd, Hg were not detected in TTW.

TWW before adsorption had Cu 1.78 µg·L^{-1}, after adsorption with WB was Cu LOQ-2.39 µg·L^{-1}. Zn was 48.27 µg·L^{-1} before adsorption, after adsorption were values lower 8.77-29.49 µg·L^{-1}. Na was 113.33 mg·L^{-1} before adsorption and 96.67-186.67 mg·L^{-1} after adsorption. Ca was 57.33 mg·L^{-1} before adsorption and 57.33-58.67 mg·L^{-1} after adsorption. Mg was 8.81 mg·L^{-1} before adsorption and 9.26-10.95 mg·L^{-1} after adsorption. Fe was 254.36 µg·L^{-1} before adsorption, after adsorption Fe was not detected. Values of Pb, Ni, Cr, As, Cd, Hg were in TWW under limit of detection.

TWW before adsorption had Cu 1.51 µg·L^{-1}, after adsorption with AFWB was Cu LOQ-1.57 µg·L^{-1}. Zn was 29.59 µg·L^{-1} before adsorption, after adsorption were values lower 9.29-21.14 µg·L^{-1}. Na was 66.67 mg·L^{-1} before adsorption and 76.67-110.0 mg·L^{-1} after adsorption. Ca was 60.33 mg·L^{-1} before adsorption and 59.0-63.0 mg·L^{-1} after adsorption. Mg was 9.31 mg·L^{-1} before adsorption, after adsorption were values lower 8.55-9.18 mg·L^{-1}. Fe was 130.84 µg·L^{-1} before adsorption, after adsorption Fe was not detected. Values of Pb. Ni, Cr, As, Cd, Hg were in TWW under limit of detection.

TWW before adsorption had Cu 1.38 µg·L^{-1}, after adsorption with GAC were values of Cu lower 0.92-1.17 µg·L^{-1}. Zn was 29.5 µg·L^{-1} before adsorption, after adsorption was Zn under limit of detection. Na was 100.0 mg·L^{-1} before adsorption and 60.0-123.33 mg·L^{-1} after adsorption. Ca was 58.0 mg·L^{-1} before adsorption, after adsorption were values lower 52.67-54.0 mg·L^{-1}. Mg was 8.8 mg·L^{-1} before adsorption and 9.08-9.48 mg·L^{-1} after adsorption. Fe was 234.12 µg·L^{-1} before adsorption, after adsorption was Fe under limit of detection. Values of Pb, Ni, Cr, As, Cd, Hg were in TWW under limit of detection.

4. Conclusion

Discharge of these TWW without pre-treatment directly into water recipient is not appropriate. Pollutants may cause the physical alteration of habitats and have direct and indirect negative effects on organisms. In the case of discharging TWW into the sewer system there is a risk of breaching the regulatory report of sewer system, that could has negative effects on treatment processes on WTP or in sewer system.
The treatment of TWW, which has proven to be more polluted and concentrated than normal road runoff, may be relatively complicated. It can be assumed to supplement the sedimentation technology with modern physical membrane technologies which may be costly or to choose a more economical technological solution consisting in filtration and adsorption on the filter medium GAC or an alternative and especially cheaper biochar. Biochar such as solution to treating TWW is in keeping with the aims of a CE strategy and the sustainability of raw products exploitation lead to search for an adequate/sustainable solution for the further usage of carbon waste and minimizing water pollution. The new knowledges of adsorbents and used concentrations and CTs may lead to future tests in road tunnels.

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