

Treatment of tunnel wash water: case study from Brno

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ABSTRACT

Tunnel wash water has been repeatedly reported to contain higher volume of pollutants, but its treatment is not legally bounded in many countries of EU and elsewhere. In this study, three samplings of tunnel wash water were carried out during 2019 and 2020. First sampling determined the chemical pollutants and helped to design the experimental tunnel wash water treatment. Second and third samplings were analysed and later treated in glasses filter pre-tests using 4 different adsorbents. As adsorbent were used food waste biochar, activated food waste biochar, wooden biochar and as the conventional adsorbent of granulated activated carbon as a control. The glasses pre-tests focused on determination appropriate contact time and amount of adsorbent. Analyses were focused on organic and inorganic pollutants contained in tunnel wash water. The results of the analysis included undissolved substances, C10-C40 hydrocarbons, chlorides, sulfates, heavy metals, and other chemical elements. The analyses showed that biochar had comparable effect on pollutants reduction such as granulated activated carbon. The adsorption had mainly effect on reducing concentration of toxic metals especially Zn (94.7%) and Cu (50.8%). The highest level of reduction was measured for Fe (98.0%). On contrary the results of tensides, sulfates and some of chemical elements showed small or none effect. For better reducing of all pollutants must precede another level of treatment. The results showed that adsorption on the filter medium could be one of treatment processes, and cheaper biochar represents an eco-friendly way of treatment tunnel wash water, which belongs among the important strategies of circular economy.

Keywords: Road tunnel; Tunnel wash water; Biochar; Heavy metals

1. Introduction

One of the main pollutions of transportation infrastructure is water pollution [1]. These effects, which stem from both construction and use, vary considerably in type and degree among regions and particular roads and tunnels [2,3]. Studies describe temporary influence during road and tunnel construction [4] and show long-time impacts of operational phase [2]. The main source of water pollution of tunnel operational phase is regular

washing, which generates large amount of tunnel wash water (TWW). This water is usually highly polluted which may cause problems at wastewater treatment plant and potentially have an acutely toxic effect for aquatic organisms [5]. In comparison of ordinary road runoff and tunnel washing, pollution of TWW is significantly higher at an otherwise similar level of traffic [6–8]. There is a lack of studies focused on treating TWW especially by adsorption on biochar or granulated activated carbon (GAC).

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At present, the management of TWW varies from country to country. In most of EU 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 [9].

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 [10].

The aim of this paper is to test the amount of pollutants in TWW, design efficient filtration apparatus with several different adsorbents, and to compare adsorbing efficiency of biochar with conventional adsorbent – GAC.

1.1. Management of TWW in EU

At present, the management of TWW varies from country to country. Of greatest concern in this issue is the fact, that the countries with the highest number of tunnels do not consider TWW treatment to be mandatory. Countries like Austria and Switzerland use sedimentation and filtration (e.g., mobile treatment trucks). However, 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. Though in the new tunnelling projects is needed to obtain a permit from the regional environmental authorities to discharge TWW [6,7].

In Switzerland and Austria is not allowed to discharge TWW untreated. In some cases, it is transported to an approved wastewater treatment plant (WWTP), but mostly TWW is drained into 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 1,400 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 WWTP.

In the Czech Republic, there are no statutory limits on the discharge of polluted TWW to recipient. The most common methods of dealing with TWW are discharging into sewer system or directly into water recipient. In sewer system TWW could exceed the set limits according to the sewer regulations and mainly these pollutants could negatively affect living organisms downstream [1,5].

Most of the pollution components in TWW are attached to particles, which can be easily removed in sedimentation basins or in ponds. However, some pollutants can still

pass through and cause toxic effects on aquatic fauna and flora [11].

1.2. Impact of TWW

During tunnel washing 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 [5,11,12]. The studies have shown that the pollutants may cause the physical alteration of habitats and have direct and indirect negative effects on organisms [1,5,8].

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 [11,13]. The frequency of washing processes ranges according to regulatory reports from 2 to 12 times/y and the volume of water ranges from 30 to 150 L per linear meter of tunnel length [8,11–14]. Washing is usually carried out by blasting surfaces with high pressurized water with or without added detergents [13,15]. The amount of used detergents is usually in the range of 0.15%–1% [8,11–13]. The water pressure ranges from 6 to 160 bar depending on the washing surface [12].

TWW typically contains a wide variety of chemical pollutants originating from vehicles, road surface, technical infrastructure such as guardrails and traffic signs and during winter season also de-icing agents [6,7,11]. In addition, the release of chemical pollutants from accidental spillages may occur [7]. Common pollutants found in TWW and their origin are reported in Table 1 [6,7].

Table 2 summarizes the maximum and minimum values reported in studies [5,13,15–18], and compares them with the maximum values set by the regulatory report for discharge of wastewater into the sewer system in the city of Brno.

The reported values that exceed the permitted limits are bolded. The maximum measured pH value of 11.77, that the TWW has an alkaline character, exceeded the set limit for discharge into the sewage system and could be caused by detergents, which contain alkaline substances [12]. The suspended solids value exceeded the permitted values by almost ten times. The limits set by the regulatory report for discharging into sewer system were further exceeded for chlorides, sulfates and phosphorus. The metals exceeded the limits for cadmium, chromium, copper, nickel, lead and zinc. These exceeded values correspond to Table 1, which lists the main indicators of substance pollution from automobile transport [5,13,15–18].

According to Table 2, TWW has increased metal concentrations which some of them are categorized as particularly hazardous and hazardous substances [9]. As a result of using 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 [1,5,8].

1.3. Biochar

Biochar is a carbonaceous material obtained from thermochemical conversion of biomass without oxygen

Table 1
Pollutants found in TWW [6,7]

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	Brakes, vehicle body, road surface (asphalt, bitumen)
Cu	Brakes, fungicides
Cd	Tire, insecticides
Cr	Vehicle body, brakes
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 2
Concentrations of selected pollutants compared with the maximum values set by the regulatory report [5,13,15–18]

	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
Chloride Cl ⁻ (mg L ⁻¹)	260	1,798	200	300
Sulfate 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	1,200	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	1,000	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	1,000	2,000

access, that is, microwave pyrolysis, or slow 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 large specific surface area, porous structure, high calorific value and enriched surface functional groups, and mineral components allowing adsorption [19–22].

The different characteristics of 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 [22].

1.4. Case study from Brno

The case study was located in one of Brno tunnels, where TWW was sampled during tunnel washing from the sedimentation tank. The applied research was focused on treating efficiency of 4 adsorbents. The efficiency was tested on selected pollutants contained in the TWW and the research was performed in laboratory conditions at AdMaS Research Centre, Brno University of Technology (BUT) in the CR. First samples of TWW were performed from tunnel washing in autumn 2019 and submitted to the Faculty of Chemistry, BUT for analysis of chemical elements. Second and third samples of TWW from spring and autumn 2020 were used for two sets of glasses filter pre-tests. The first set of glasses pre-tests was used to determine the appropriate contact time (CT) of TWW and adsorbents, and the second set was focused on determining the amount of adsorbent. As adsorbents were used granulated activated carbon, food waste biochar, activated food waste biochar and wooden biochar. Analyses of second and third samples of TWW were focused on undissolved substances, C10-C40 hydrocarbons, chlorides, sulfates, heavy metals, and chemical elements. For comparing of adsorbents efficiency, the analyses were performed before and after adsorption.

2. Material and methods

For experiments three samples of TWW from the road tunnel in Brno were used. The washing is regulated by the administration of the Directorate of Roads and Motorways of the Czech Republic and 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, and pressurized water is used only for washing the tunnel lining. In the tunnel TWW flows through street drains into the sedimentation tank and into sewer system [14].

Tunnel has two tubes, each of it has two lines. The total length of road tunnel is 2495 m and annual average daily traffic is 30,000. Total water consumption during one washing is 400 m³. The average water consumption is 160.3 L per linear metre of tunnel, including the ceiling, tunnel lining, sidewalk, road, and all equipment.

To simulate the process of filtration in a tunnel sedimentation tank, the TWW was experimentally treated by four adsorbents: food waste biochar (FWB), activated food waste biochar (AFWB), wooden biochar (WB) and granulated activated carbon (GAC). WB is the best known and commonly used biochar, contrary to FWB is renewable and could lead to reducing waste dumping. FWB and AFWB were produced by medium-temperature pyrolysis. The efficiency of biochar adsorbing was compared to a conventional adsorbent – GAC.

2.1. Preparing of activated biochar

The specific surface area of the food waste biochar (FWB) was increased by activating, with concentrated hydrochloric acid HCl according to Fig. 1.

Prior to the activation, the biochar pellets were crushed and sieved to the required fraction of 0.5–2.0 mm. Upon activation, the entire surface of the biochar was in contact with concentrated HCl for 24 h [23]. After the 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 h. 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 h [24].

2.2. TWW sample preparation

TWW for laboratory testing purposes was pumped from the sedimentation tank into the prepared Intermediate bulk containers (IBC), during tunnel washing in autumn 2019 and in spring and autumn 2020.

The samples of fresh TWW from tunnel washing in autumn 2019 were submitted for chemical analysis. Analyses were focused on following chemical elements: Cu, Pb, Ni, Cr, As, Cd, Zn, Na, Ca, Mg and Fe.

The samples of TWW from tunnel washing in spring and autumn 2020 were tested with 4 different adsorbents and phased to two steps which is illustrated in Fig. 2.

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 L⁻¹. The samples were placed in thermostat cabinets and stirred at a constant temperature of 23.0°C–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 pouring 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, 2.5 and 4.0 g L⁻¹. The samples were placed in thermostat cabinets and stirred at a constant temperature of 20.5°C–23.0°C for 1 h.

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 (µS cm⁻¹) and specific resistance (Ω cm) were measured.

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

2.3. Determination of pH, EC, TDS and S_{BET} specific surface area

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



Fig. 1. Schema of preparing activated biochar.

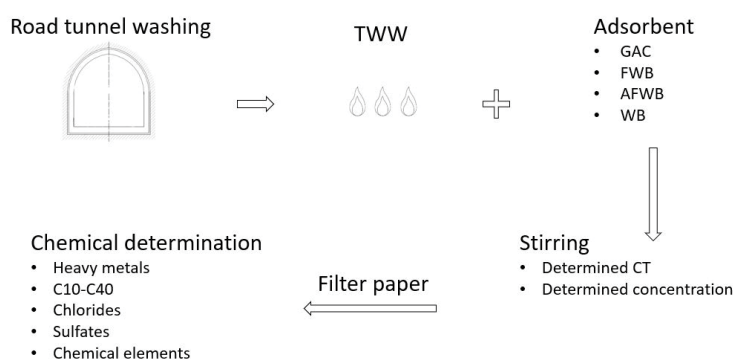


Fig. 2. Schema of glasses pre-test.

The specific surface area (S_{BET}) of the adsorbents (g 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 h at 150°C .

2.4. Chemical analysis

2.4.1. Determination of chemical elements

For the determination of chemical elements contents were performed using an 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 $20 \mu\text{L}$. Table 3 shows limit of detection and qualification for each of measured elements.

All obtained results are the average of three separate independent determinations, each was measured for atomic absorption spectrometer three times.

2.4.2. 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 h. 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 $30^\circ\text{C min}^{-1}$ to 320°C , 320°C for 15 min. For calibration was used mineral oil in n-heptane in concentrations of $0.2\text{--}400 \text{ mg L}^{-1}$.

3. Results and discussion

The first section describes results of fresh samples from tunnel washing in autumn 2019. Analyses were focused to the following chemical elements: Cu, Pb, Ni, Cr, As, Cd, Zn, Na, Ca, Mg and Fe. Values are based on 1 grabbed sample.

The second and third section describe results from 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. Values are based on 1 grabbed sample.

Table 3
Determined LOD and LOQ for measured elements

Element	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	Element	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)
As	3.756	11.27	Mg	1.578	4.7
Ca	15,000	–	Na	200	–
Cr	0.9853	2.956	Ni	2.169	6.5
Cu	0.29	0.875	Pb	2.385	9.69
Fe	5.024	16.748	Zn	1.578	4.7
Hg	0.774	2.579	–	–	–

LOD – limit of detection, LOQ – limit of qualification.

3.1. Chemical analysis of TWW from tunnel washing in autumn 2019

The results of chemical analysis of fresh TWW from tunnel washing in autumn 2019 are reported in Table 6. All samples were not sedimented and no adsorbent was added, regarding to chemical analysis all samples were filtered through the filter paper before analyses.

According to Table 4, the values of measured chemical elements were lower than the maximum values set by the regulatory report for discharging of wastewater into the sewer system in the city of Brno described in Table 2.

According to Table 4, TWW sampled in autumn 2019 had comparable values of elements as the studies showed [5] and also with values measured in samples from washing in spring and autumn 2020 as can be seen in Tables 6 and 8. Significant difference was in content of Ca and Zn. Content of Ca was 10 times smaller than results showed in Tables 6 and 8 and Zn was under limit of detection.

3.2. Glasses pre-tests – CT, TWW from tunnel washing in spring 2020

The results of TWW composition from spring washing before and after adsorption are reported in tables below. Three adsorbents were used: GAC, FWB, and AFWB.

Concentrations of adsorbents were for all samples the same 2.5 g L^{-1} . Tested CTs were 0–7–24–46 h. All samples were filtered through the filter paper before analyses.

Table 5 shows measured parameters: S_{BET} , pH, temperature, oxidation–reduction potential, salinity, EC, TDS, spec. ρ , C10–C40, and chlorides.

According to Table 5, measured values of S_{BET} were significantly higher for GAC than for FWB and AFWB. 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.

TWW had similar results of EC, TDS and spec. ρ before and after adsorption with GAC and AFWB, after adsorption with FWB were results different.

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, which is in accordance with concentration of chlorides.

As it can be seen, the concentration of chlorides in TWW before adsorption was $4,100 \text{ mg L}^{-1}$, after adsorption with FWB concentration was increasing and ranged $4,100\text{--}4,600 \text{ mg L}^{-1}$.

The following Table 6 describes concentrations of selected parameters: Cu, Pb, Ni, Cr, As, Cd, Zn, Na, Ca, Mg, Fe, and Hg.

According to Table 6 none of the measured samples exceeded maximum limits set by the regulatory report for discharging into the sewer system in the city of Brno as it can be seen in Table 2. Measured values of untreated TWW were in the range described in studies and summarized in Table 2 [5,13,15]. Values of Cr, As, Pb, Cd, Fe, Hg were in TWW under the limit of detection.

The concentration of Zn in untreated TWW exceeded limit defined by standards for surface water quality and protection of aquatic life in freshwater [25]. Comparable values of pollutants in TWW after adsorption with another study [11] and the most effective results were measured for Zn. Before adsorption with GAC was concentration of Zn $21.36 \mu\text{g L}^{-1}$ and $4.1\text{--}10.97 \mu\text{g L}^{-1}$ after adsorption. Zn was $141.82 \mu\text{g L}^{-1}$ before adsorption with FWB and after adsorption were values lower $8.55\text{--}13.06 \mu\text{g L}^{-1}$ and after adsorption with AFWB were values $16.76\text{--}27.57 \mu\text{g L}^{-1}$.

Table 4
Chemical elements in TWW from tunnel washing in autumn 2019

Element	Sample n. 1 ($\mu\text{g L}^{-1}$)	Sample n. 2 ($\mu\text{g L}^{-1}$)	Sample n. 3 ($\mu\text{g L}^{-1}$)
As	<LOD	<LOD	<LOD
Ca	5,000	5,200	52,00
Cd	0.144	0.149	0.121
Cr	8.416	10.944	6.758
Cu	27.228	26.473	26.959
Fe	111.820	111.580	118.600
Mg	15,750	15,831	15,646
Na	220,000	230,000	200,000
Ni	9.128	6.967	6.808
Pb	<LOD	<LOD	<LOD
Zn	<LOD	<LOD	<LOD

Table 5
 TWW composition from spring washing and after adsorption: S_{BET} , EC, TDS, spec. ρ , C10-C40, and chlorides

Adsorbent	Time (h)	Weight (g L^{-1})	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	pH	Temperature ($^{\circ}\text{C}$)	ORP (mV)	Salinity	EC ($\mu\text{S cm}^{-1}$)	TDS (mg L^{-1})	spec. ρ (Ωcm)	C10-C40 (mg L^{-1})	Chlorides (mg L^{-1})
GAC	0	0		7.961	26.8	168.4	0.9	1,837	1,837	544	15.65	–
	7	2.5	610.93	8.574	25.3	139.0	0.9	1,870	1,869	535	15.75	–
	24	2.5		8.791	24.9	97.2	0.9	1,869	1,869	535	14.65	–
	46	2.5		8.883	24.6	165.0	0.9	1,880	1,880	532	8.17	–
FWB	0	0		7.906	17.8	198.5	0.9	1,801	1,801	555	5.08	4,100
	7	2.5	1.21	8.778	19.1	160.5	1.1	2,180	2,180	459	4.52	4,100
	24	2.5		8.815	23.2	167.9	1.1	2,240	2,240	446	6.79	4,150
	46	2.5		8.918	23.3	168.0	1.1	2,200	2,200	455	4.54	4,600
AFWB	0	0		7.906	17.8	198.5	0.9	1,801	1,801	555	5.08	4,100
	7	2.5	2.85	8.366	19.8	197.7	0.9	1,855	1,855	539	4.20	4,050
	25	2.5		8.604	24.9	193.5	0.9	1,850	1,850	540	4.90	4,050
	46	2.5		8.680	24.9	166.1	0.9	1,880	1,880	532	4.71	3,850

GAC – granular activated carbon; FWB – food waste biochar; AFWB – activated food waste biochar; S_{BET} – surface area; 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.

Table 6
 TWW composition from spring washing and after adsorption: Cu, Ni, Cr, As, Zn, Na, Ca, Mg

Adsorbent	Time (h)	Weight (g L ⁻¹)	Cu (µg L ⁻¹)	Ni (µg L ⁻¹)	Cr (µg L ⁻¹)	As (µg L ⁻¹)	Zn (µg L ⁻¹)	Na (mg L ⁻¹)	Ca (mg L ⁻¹)	Mg (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

GAC – granular activated carbon; FWB – food waste biochar; AFWB – activated food waste biochar; LOD – limit of detection; LOQ – limit of qualification.

Table 7

TWW composition from autumn 2020 washing and after adsorption: S_{BET} , pH, US, tenside, C10-C40, chlorides, and sulfates

Adsorbent	Weight (g L ⁻¹)	S_{BET} (m ² g ⁻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
	0.0		8.397	0.45 (UF)	0.14	0.13 (UF)	220.00	62.00
WB	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
	0.0		8.395	0.42 (UF)	0.31	0.64 (UF)	185.00	73.00
AFWB	1.0	2.85	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
	0.0		8.288	0.16 (UF)	0.25	0.05 (UF)	225.00	63.00
GAC	1.0	610.93	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

US – undissolved substances; WB – wooden biochar; AFWB – activated food waste biochar; GAC – granular activated carbon; UF – unfiltered samples; F – filtered samples.

On contrary the concentration of Na increased after adsorption with FWB, these results respond with values of salinity and chlorides shown in Table 5. The values increased with longer CT; after 46 h, the concentration of Na was 36% higher than in the samples before adsorption. The concentration increase was probably related to the source of biochar, which was food waste from restaurants containing table salt. According to the results of Na was FWB precluded from second set of glasses pre-tests.

Content of selected parameters were significantly lower after 7 h of CT and results showed that longer CT had low efficiency, that is the reason why in second set of glasses pre-tests was chosen CT 1 h. Results also showed comparable efficiency of biochar and conventional adsorbent – GAC.

3.3. Glasses pre-tests – adsorbent concentration, TWW from tunnel washing in autumn 2020

The results of TWW composition from autumn washing before and after adsorption are reported in tables below. Three adsorbents were used: WB, AFWB, and GAC. Tested concentrations of adsorbents were 1.0, 2.5, and 4.0 g L⁻¹. CTs were for all samples the same 1 h.

TWW composition from autumn washing before and after adsorption is reported in Table 7. The samples described unfiltered samples (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. These selected parameters were measured: S_{BET} , pH, US, tenside, C10-C40, chlorides, and sulfates.

According to Table 7, TWW analysed immediately after tunnel washing without treatment had concentration of

chlorides exceeded limit defined by standards for surface water quality and protection of aquatic life [25].

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.

These selected parameters are reported in Table 8. The sample without adsorbent was analysed immediately after tunnel washing, the rest of samples were analysed after 5 months because of absence of adsorbents. All samples were filtered through the filter paper before analyses.

In TWW analysed immediately after tunnel washing was found the value of Zn, which exceeded limit defined by standards for surface water quality and protection of aquatic life [25]. Pb, As, Cd, Hg were not detected in TWW.

Table 8
TWW composition from autumn 2020 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

WB – wooden biochar; AFWB – activated food waste biochar; GAC – granular activated carbon; LOD – limit of detection; LOQ – limit of qualification.

According to Table 8, none of the measured samples exceeded maximum limits set by the regulatory report for discharging into the sewer system in the city of Brno as it can be seen in Table 2. Measured values of untreated TWW were in the range described in studies and summarized in Table 2 [5,13,15]. Values of Pb, Ni, Cr, As, Cd, Hg were in TWW under the limit of detection. Comparable efficiency of adsorption with another study [11] was measured for Zn and Fe.

The highest efficiency was measured for Fe. Before adsorption with WB was concentration of Fe 254.36 µg L⁻¹ and after adsorption with all doses of WB was Fe not detected, which means that concentration of Fe was lower than 5.024 µg L⁻¹ and efficiency of adsorption was almost 98.0%. Before adsorption with AFWB was Fe 130.84 µg L⁻¹ and after adsorption was Fe not detected and efficiency of adsorption was 96.2%. Fe was not detected after adsorption with GAC and efficiency of adsorption was 97.9%.

Concentration of Zn was measured in range 29.5–48.27 µg L⁻¹ before adsorption. After adsorption with GAC Zn was not detected for all doses, which means that concentration was lower than 1.578 µg L⁻¹. After 1 h adsorption

with 1 g L⁻¹ of AFWB was concentration 9.29 µg L⁻¹ and efficiency of adsorption was almost 70%. After 1 h adsorption with 1 g L⁻¹ of WB was concentration 8.77 µg L⁻¹ and efficiency of adsorption was 82%.

Concentration of Cu was measured in range 1.38–1.78 µg L⁻¹ before adsorption. After 1 h adsorption with 1 g L⁻¹ of WB and AFWB was Cu under limit of quantification, which means that concentration was lower than 0.875 µg L⁻¹.

Content of selected parameters were significantly lower after 1 h of CT with dose of adsorbents 1 g L⁻¹ and results showed that higher concentration of adsorbent had low efficiency, that is the reason why in future testing will be used more adsorbents with dose of 1 g L⁻¹ and CT 1 h. Results also showed comparable efficiency of biochar and conventional adsorbent – GAC.

4. Conclusion

This study has confirmed that TWW has higher concentrations of pollutants than normal road runoff and contains particularly hazardous and hazardous substances.

The chemical analyses have even shown the exceeded limit defined by USEPA standards for surface water quality and protection of aquatic life for Zn and chlorides.

The first set of glasses pre-test showed that the tested adsorbents effectively removed mainly Zn and significant results were after CT 7 h. That was the reason, why in the second set of glasses pre-test was CT 1 h. On contrary, the results showed increasing concentration of Na and chlorides after adsorption with FWB, that was caused by source of biochar. The second set of experiments verified the results of Zn and showed even better results of Fe. All chosen adsorbents reduced Fe concentration to level below limit of detection even with concentration of adsorbents 1 g L⁻¹. The glasses experiments showed significant reducing of toxic metals especially Zn and Cu. However, the obtained results showed that adsorbents had small effect on reducing concentration of Na, Ca and Mg and for reducing have to precede another level of treatment.

The experimental treatment with selected filtration materials has shown that biochar produced from different waste materials has great potential to filtrate TWW efficiently, especially in terms of Fe, Zn and Cu. The obtained results from the glasses pre-tests showed that biochar was comparable efficient in the treatment of TWW as GAC. Thus, we can conclude that TWW requires more comprehensive treatment and biochar torrefacted from food waste or wood production waste might be considered equivalent to the conventional GAC which is on the other hand produced from primary sources and thus does not conform the principles of circular economy.

Further investigations and studies focused on treatment system are required, TWW represents a comprehensive spectrum of traffic pollution that contains hazardous substances which can cause direct and indirect negative effects on organisms.

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