

## Properties of Reactive Materials for Application in Runoff Water Treatment Systems

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### ABSTRACT

The emissions related to urbanized areas, including communication routes and accompanying facilities, are considered as essential sources of subsoil pollution. Enhancement of the naturally occurring removal processes in infiltration systems, e.g. through placing the appropriately selected materials (treatment zones) on the flow path of runoff water, prevents the spread of undesirable components. The article presents the analysis of tests checking the properties of selected low-cost mineral materials, activated carbon and zero-valent iron in terms of their applicability in the runoff water treatment zones. Their physical features, surface structure, and chemical and hydraulic properties were analysed. The test results indicate a well-developed surface area of active carbon and halloysite, as well as an extensive pore volume of active carbon, halloysite, zeolite and diatomite. Nevertheless, the average pore diameters indicated the potential limited access of pollutants to the inner structure of all analyzed materials. The chemical parameters point to the stimulation potential of precipitation processes by limestone sand and silica spongolite, ion exchange by zeolite and silica spongolite, and oxidation-reduction processes by zero-valent iron. The value of the material hydraulic conductivity may potentially limit their application in infiltration systems. Taking into account all analyzed parameters, activated carbon together with silica spongolite and zeolite have the best application potential.

**Keywords:** infiltration system, contaminants removal, physico-chemical properties, hydraulic properties

### INTRODUCTION

Systematic increase in area of economically used land is closely correlated with the increase of impermeable surfaces, on which progressively larger volumes of runoff water are generated. Water carries the pollutants emitted during the exploitation of urban areas (heavy metals, organic compounds, mainly petroleum substances and polycyclic aromatic hydrocarbons, biogens, dissolved salts, and suspensions) that, consequently, are driven to water receivers, e.g. to the soil/water system (Nawrot and Wojciechowska 2018). Currently, the runoff water is a problem not only due to its volume, but also its quality. Thus, it is important both to manage the runoff water in accordance with the principles of sustainable development in order to increase its local retention, as well as to protect all components of the environment. As such, special elements of the drainage

system, e.g. separators, settlers, filter strips and swales, infiltration systems and wetlands, can be installed to ensure the appropriate quality of the runoff water discharged into the environment (Hilliges et al. 2013, Xu et al. 2020). Particularly noteworthy are the solutions treated as one of the elements of best management practice (BMP), known as permeable treatment zones (elements of infiltration systems) filled with the specially selected natural and synthetic materials (Fronczyk 2017, Valencia et al. 2020). The initial selection of materials involves the analysis of basic laboratory tests. However, the choice of the material, or possibly several materials constituting a mixture or forming a layered system, should be made considering the type of contaminants, their concentration and form (state) at which they are present in the natural environment.

In addition to the parameters directly characterizing the sorption rate and capacity of

materials, which include, e.g. the maximum sorption capacity and constant reaction rates, there are a number of techniques that allow drawing indirect conclusions on the suitability of a given material for its use in the treatment of aqueous solutions. These include the analysis of material morphology, material surface chemistry, hydrophobicity, textural properties, crystalline structure, physicochemical parameters and hydraulic properties (Tran et al. 2017).

Scanning electron microscopy (SEM) allows for the observation of the surface and sub-surface areas on nano- and micrometric scales, and when the test is combined with the analysis of X-ray energy dispersion (EDS) – also the observation of the chemical composition (Stokes, 2008). On the basis of SEM images, one can conclude on the material porosity, the pore specific surface area, the shape and dimensions of pores, and the occurrence of specific forms such as nanotubes characteristic of halloysite. The SEM images, together with BET specific surface area, total pore volume, as well as micro- and mesopore volume allow drawing conclusions on the sorption capacity of materials and the availability of pores for the interaction with specific contaminants (Yong and Mulligan 2004). Additionally, a larger percentage of micropores in the total pore volume may have a positive effect on the sorption capacity of materials in relation to small particles of contaminants (Tran et al. 2017). The pore dimensions play a significant role in the classification of some materials (e.g. zeolites, including primarily synthetic zeolites, and activated carbon) as molecular sieves that are used in the selective retention of chemical molecules (Shimizu et al. 2018). Moreover, the surface properties influence the cation exchange capacity (CEC) related to the quantity of negatively charged sites on the surface that retain exchangeable cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ). According to Khorshidi and Lu (2017), learning about this property of the material primarily facilitates the assessment of the processes responsible for removing contaminants as a result of ion exchange, but also implies water sorption, hydraulic conductivity and contaminant migration. On the other hand, the mineralogical composition determines the pH and oxidation-reduction potential (ORP) of a given material, which controls not only the ionic state of the functional groups on the surface of reactive materials that take part in binding contaminants, but also the speciation of heavy

metals affecting their availability, precipitation, complexation by ligands, hydrolysis and redox reactions (Lodeiro et al. 2006).

The grain-size distribution of materials plays an important role in controlling the velocity of the contaminated water flow and thus the efficiency of treatment processes, because it influences hydraulic conductivity – a parameter defining the ability of a porous medium to conduct liquids. However, the parameter may be affected by many other factors, such as mineral composition, degree of saturation, porosity, as well as the shape and texture of the surface of solid particles (Head and Epps 2011). Parylak et al. (2013) indicated lower values of hydraulic conductivity for the materials characterized by a complex shape and surface structure compared to the materials with uniform shapes (glass balls), which was explained by the retention of larger amounts of water bound in microcavities. Likewise, the empirical Kozeny-Carman equation for the hydraulic conductivity of porous media (Carman 1937, Kozeny 1927) links this parameter with the porosity and specific surface area related to the volume of the medium. The results of calculations presented by Yong and Mulligan (2004) show a negative correlation between the specific surface area of the porous medium and the value of hydraulic conductivity.

To summarize, the properties of materials mentioned above determine both the treatment processes and the efficiency of contaminant removal in the soil/water environment, and thus may play a significant role in the treatment of the runoff water generated in urbanized areas. The primary objective of this study was to examine the materials (commonly referred to as reactive materials) that could be used as structural layers enhancing the processes of contaminant removal, naturally occurring in the soil/water environment. The paper presents an assessment of the selected reactive materials resulting in the preparation of a materials ranking for their potential application as the filling material of treatment zones in runoff water treatment systems.

## MATERIALS AND METHODS

### General characteristics of selected materials

Assuming the contaminant mixture in the runoff water from road infrastructure, the study

focused on the properties of the following materials: zero-valent iron – ZVI (iPutec GmbH & Co. KG, Rheinfelden, Germany), activated carbon (Activated Carbon Research and Production Plant, Mrozy, Poland), zeolite (N. Hrabovci, Zeocem S.P., Bystre, Slovakia), silica spongolite (“Góra Maćkowa” deposit, Polskie Górnictwo Skalne Minerał, Wrzosówka, Poland), limestone sand (Chatkowice deposit, Przedsiębiorstwo Górniczych “SILESIA” Sp. z o.o., Czechowice-Dziedzice, Poland), diatomite (“Jawornik Ruski” deposit, Specialist Mining Enterprise “Górtch”, Wieliczka, Poland) and halloysite (“Dunino” deposit, PTH InterMag, Gliwice, Poland). Most of the selected materials belong to the group of natural minerals available in Poland, which are used, e.g., in the treatment technologies of the water and soil environment (Figarska-Warchoł et al. 2015, Radziemska and Mazur 2017, Radziemska 2018). Only zeolite came from a deposit located in Slovakia, because in Poland there are only deposits of clinoptilolite-montmorillonite clay, in which the content of clinoptilolite is less than 30% (Kłapyta and Żabiński 2008). Additionally, activated carbon and zero-valent iron were selected as reference materials due to their wide use in groundwater treatment with the permeable reactive barrier (PRB) method (Gillham and O’Hannesin, 1994, Feng et al., 2016). It is also worth mentioning that these reference materials are expensive compared to common mineral materials. The retail prices (per 100 kg) of activated carbon and ZVI are 1050 PLN and 750 PLN, respectively, while for mineral materials – in the range of 11 PLN (silica spongolite) to 150 PLN (diatomite). Therefore, mineral materials can be called low-cost materials; thus, in consequence, their application may be of great importance when designing systems for treating runoff water from urban areas due to the installation costs.

### Test methods

The test methods of the physicochemical properties, surface structure and the hydraulic properties of the reactive materials are presented in Figure 1. The tests of physicochemical and hydraulic properties were carried out in at least three repetitions, based on which the average values were calculated.

## TEST RESULTS

### Physical properties and surface structure

The most complex surface with a porous character has the activated carbon sample, while the least complex pore structure has the ZVI sample (Figure 2a), which is also reflected in the smallest specific surface of this material (Figure 3a). SEM images have also indicated a moderately developed surface of diatomite, zeolite and halloysite, as well as a poorly developed surface of silica spongolite and limestone sand.

On the basis of the results of nitrogen adsorption/desorption tests, the tested materials can be subdivided into three groups: (1) microporous material – activated carbon with a total specific surface area of 782.67 m<sup>2</sup>/g and a micropore surface area of 366.41 m<sup>2</sup>/g; (2) mesoporous materials with moderately developed specific surface – diatomite with a specific surface area of 29.32 m<sup>2</sup>/g, zeolite with a specific surface area of 33.34 m<sup>2</sup>/g, and halloysite with a specific surface area of 48.33 m<sup>2</sup>/g (Fronczyk and Mumford 2019); (3) non-porous materials – silica spongolite (2.82 m<sup>2</sup>/g) (Pawluk and Fronczyk 2015), limestone sand (0.91 m<sup>2</sup>/g), and zero-valent iron (0.52 m<sup>2</sup>/g) (Fronczyk 2017) (Figure 3a). The characteristics of the porous structure based on the average pore size (Figure 3b) allow the materials to be arranged in descending order of pore diameter as follows: zeolite > halloysite > ZVI > limestone sand > silica spongolite > diatomite ≥ activated carbon. The maxima on the diagram of pore volume distribution (Figure 2b) show the presence of micropores at 0.41 nm and 0.5 nm in diameter for activated carbon and mesopores at 4.02 nm in diameter for diatomite, at about 4 nm and in the range of 7.5–20 nm in diameter for zeolite, and at 4 nm and 6 nm in diameter for halloysite. The values of pore volume and pore volume distribution (PVD) of silica spongolite, limestone sand and zero-valent iron have indicated a negligible number of pores, or lack thereof.

The test of mineral composition by diffraction analysis showed the amorphous character of activated carbon and the complementation of this material by quartz. The main mineral group containing diatomite is the silica group (chalcedony/CT-opal) with clay minerals represented by smectite, illite, kaolinite, feldspar and quartz, which allows the material to be classified petrographically as diatomaceous earth. Silica spongolite and

Physical properties and surface structure	surface morphology	scanning electron microscopy (FEG Quanta 250, USA)
	specific surface area	nitrogen adsorption at 77 K,
	pore diameters	BJH method (ASAP 2020M Micromeritics, USA)
	total pore volume ( $V_{total}$ )	for activated carbon: t-Plot micropores analysis and Horvath-Kawazoe method for micropores volume distribution
	mineral composition	powder method (Philips X'pert APD X-ray diffractometer, with a PW 3020 goniometer, Cu lamp and a graphite monochromator, Netherlands) (5-65 $2\theta$ angle range, JCPDS - ICDD database)
	specific density	pycnometric method (PN-EN ISO 17892-3:2016-03)
	particle size distribution	sieve and areometric methods (PN-EN ISO 17892-4:2017-01)
Chemical properties	oxide composition	energy dispersive X-ray fluorescence XRF (Epsilon-3 spectrometer (Panalytical), Rh X-ray tube (9 W, 50 kV, 1 mA), 4096-channel spectrum analyzer, 6 measuring filters (Cu-500, Cu-300, Ti, Al-50, Al-200, Ag) and the highresolution solid state SDD detector (50 $\mu$ m thick beryllium window), cooled with a Peltier's cell)
	electrolytic conductivity, pH, and ORP	in aqueous suspensions in the proportions 1: 2.5 (w/v) and 1: 5 (w/v) respectively using a multi-parameter meter pH/LF 12 (Schott, Germany)
	cation exchange capacity	at pH 7 with ammonium acetate (Schollenberger and Dreibelbis 1930)
Hydraulic properties	hydraulic conductivity	constant gradient method ( $i = 1.8$ ) using tap water at 15°C, converting the results for a standard temperature of 10°C (ASTM D7100 - 11(2020))
	hydrophobicity	based on the water drop penetration time, interpretation based on the threshold times (Roberts and Carbon 1971)

**Figure 1.** Scheme of the methodology used in this study

limestone sand can be assigned to the limestone group of minerals because of calcite ( $\text{CaCO}_3$ ) being the main mineral component. Halloysite was confirmed to be the main component of the mineral from the “Dunino” deposit, together with goethite, hematite and microcline. The main component of the selected zeolite is clinoptilolite with admixtures of quartz and illite. The test results for zero-value iron illustrated the homogeneity of this material in mineralogical terms (Fe).

The tests confirmed that the lightest material is activated carbon ( $\rho_s=1.96 \text{ Mg/m}^3$ ) and the heaviest is zero-valent iron ( $\rho_s=7.80 \text{ Mg/m}^3$ ) (Figure 4a). Among mineral materials, diatomite was characterized by the lowest specific density, and limestone and silica spongolite by the highest density, for which this parameter had the same value. The specific density of mineral materials (in the range of 2.17 to 2.71  $\text{Mg/m}^3$ ) allows

classifying them as ordinary aggregates. A probable explanation is the similar origin, similar crystal structure, as well as surface morphology and oxide composition of these materials.

### Chemical properties

The oxide composition of the reactive materials is presented in Figure 5. In the activated carbon sample, in addition to the predominant component, i.e. carbon, silicon dioxide ( $\text{SiO}_2$ ) was observed, followed by aluminum oxide ( $\text{Al}_2\text{O}_3$ ), iron (III) oxide ( $\text{Fe}_2\text{O}_3$ ), calcium oxide (CaO) and sodium oxide ( $\text{Na}_2\text{O}$ ). Zero-valent iron consists of iron (III) oxide, which accounts for 98.95%. The percentage of the remaining components was lower than 1%. The dominant component of halloysite and zeolite was silicon dioxide followed by aluminum oxide and additionally iron (III)

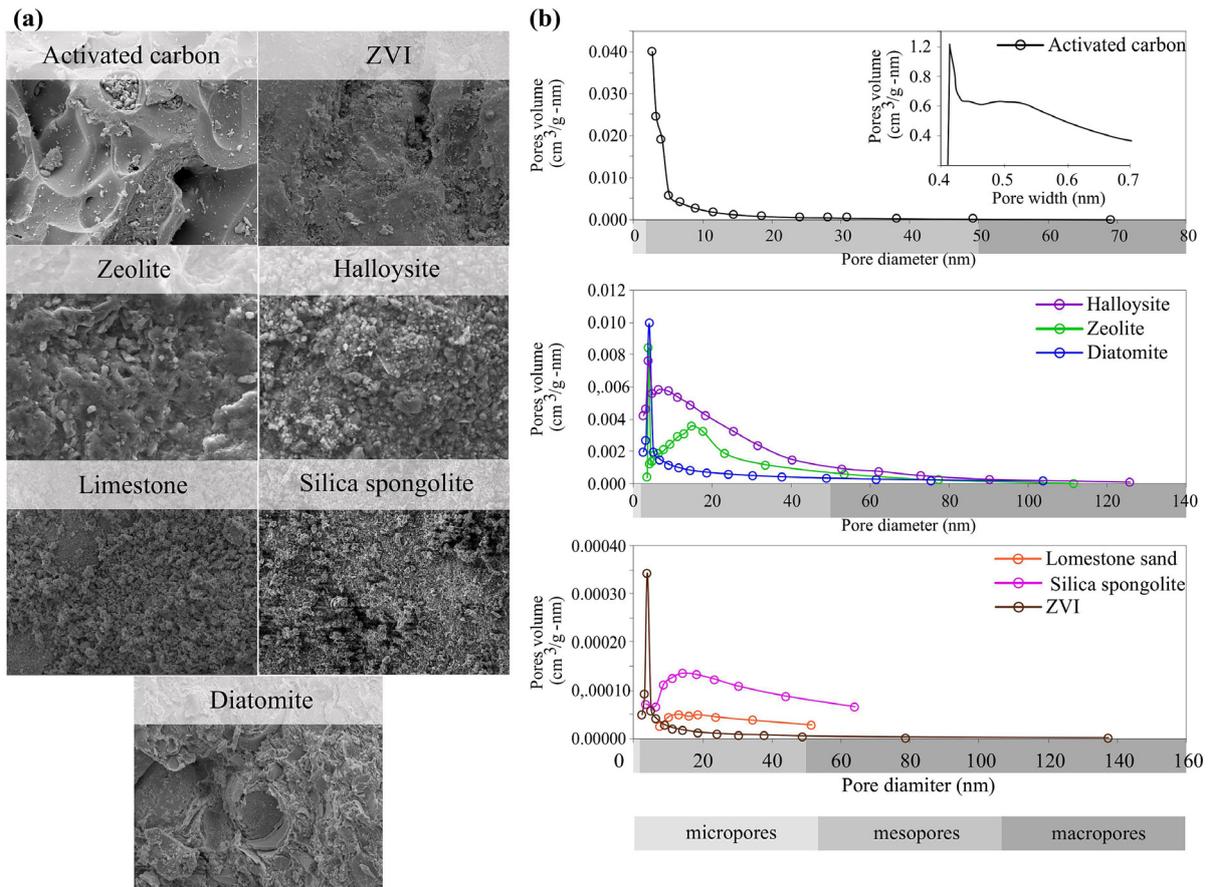


Figure 2. SEM images (2000 x magnification) (a), and distribution of pore volume relative to their diameter (additionally, for activated carbon, the distribution of micropore volume relative to their width) (b)

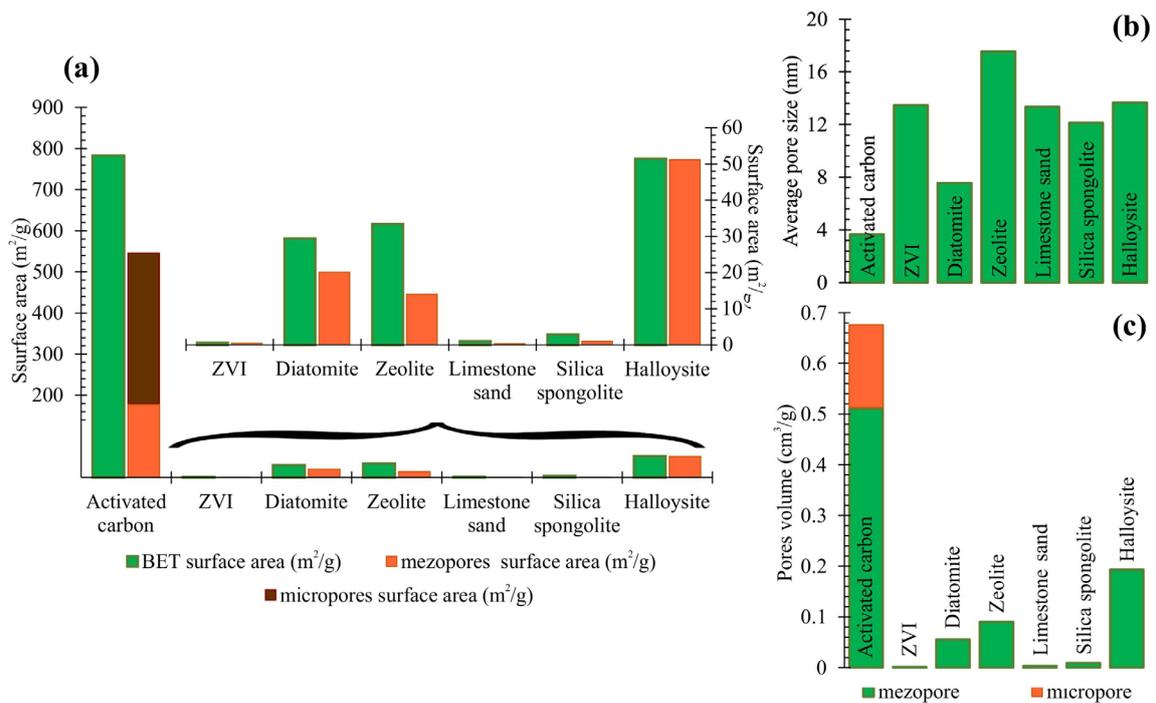


Figure 3. Specific surface area (a), average pore size (b), and pore volume (c) of the reactive materials tested

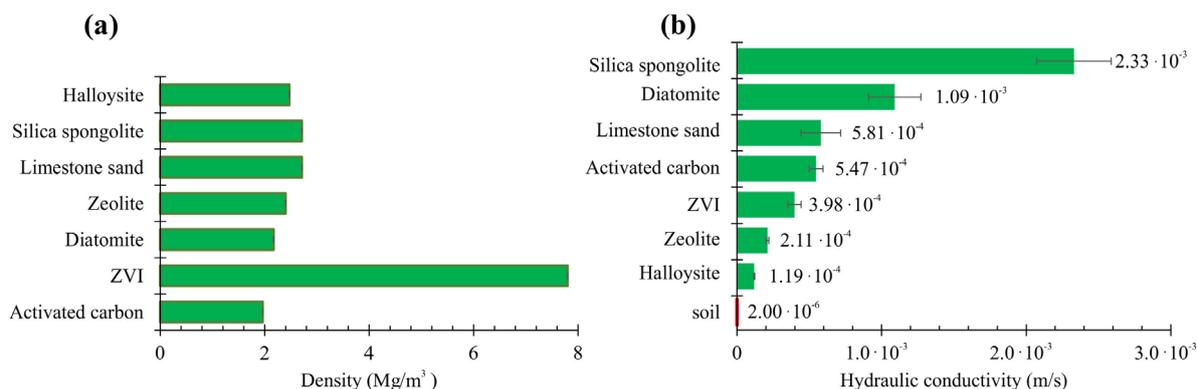


Figure 4. Average specific density values (a), and hydraulic conductivity (b) (mean value and standard deviation for n = 5)

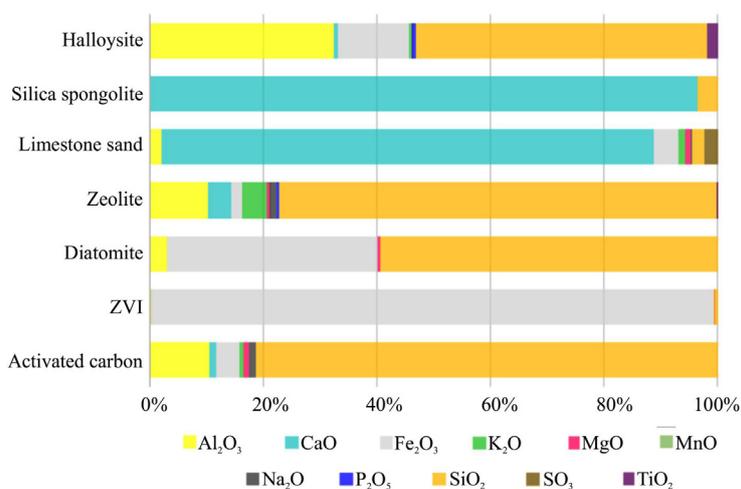


Figure 5. Oxide composition of the reactive materials tested

oxide for diatomite. Zeolite in its oxide composition contained over 1% of K<sub>2</sub>O, CaO and Fe<sub>2</sub>O<sub>3</sub>, halloysite – of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, and diatomite – of Al<sub>2</sub>O<sub>3</sub> and C<sub>2</sub>O. The studies on the oxide composition of limestone sand and silica spongolite also indicated the similarity of these materials. The main component of these materials is calcium oxide (CaO), which accounts for 82.54% in limestone sand and 96.5% in silica spongolite. Limestone sand (above 1%) additionally includes

Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, while silica spongolite contains also SiO<sub>2</sub>.

The reactive materials tested are characterized by a wide range of pH, from slightly acidic (pH = 6–7) in the case of diatomite and halloysite, through slightly alkaline (pH = 7–8) for zeolite, silica spongolite and ZVI, to alkaline (pH > 8) for limestone sand and activated carbon (Table 1), which is influenced by the mineralogical composition of the materials. The (slightly) alkaline pH of silica spongolite and limestone sand is influenced

Table 1. The pH, electrical conductivity, oxidation-reduction potential, and cation exchange capacity of the reactive materials tested

Material	Activated carbon	ZVI	Diatomite	Zeolite	Limestone sand	Silica spongolite	Halloyzite
pH	8.68*	7.85	6.48*	7.2*	8.27*	7.74	6.58*
EC (µS/m)	0.620*	0.068	0.103*	0.187*	0.095*	0.518	0.270*
ORP after 24 h (mV)	74.7	-29.5	184.6	79.1	50.3	83.3	141.3
CEC (meq/100g)	5.97*	-	13.88*	118.02*	1.11*	77.61	10.76*

\* Fronczyk and Mumford 2019

by the content of calcium carbonates, while that of activated carbon is likely to be the activation using base reagents. The determined values of electrolytic conductivity of the materials also show a large variation in the range from 0.068  $\mu\text{S}/\text{m}$  for ZVI to 0.620  $\mu\text{S}/\text{m}$  for activated carbon (Table 1). Out of the mineral materials, limestone sand has the lowest electrolytic conductivity (0.095  $\mu\text{S}/\text{m}$ ) and the largest – silica spongolite (0.518  $\mu\text{S}/\text{m}$ ). Moreover, the ORP of all mineral materials and activated carbon had positive values, only ZVI had a negative value of this parameter.

### Particle size and hydraulic properties

On the basis of the particle size distribution tests, the characteristic values of effective diameters ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$ ), coefficient of uniformity  $C_U$  ( $d_{60}/d_{10}$ ) and coefficient of curvature  $C_C$  ( $d_{30}^2/(d_{10} \cdot d_{60})$ ) were determined (Table 2). The mineral materials tested were created as a result of mechanical fragmentation of the rocks, which is why they are characterized by grains with sharp edges and rough surfaces. The largest variability in particle size was observed in silica spongolite (from 0.2 to 3.15 mm) and the lowest – in halloysite, zeolite and limestone sand (from 0.2 to 1.0 mm). It also reflects the percentage of fractions smaller than 0.5 mm, on the basis of which materials can be arranged in the following increasing order: diatomite < activated carbon  $\approx$  zero-valent iron < silica spongolite < zeolite  $\ll$  halloysite < limestone sand. Additionally, capillary rise was determined on the basis of the material particle size distribution using the equation for pure water  $h_c = 15.3/r$ , where  $r$  is the mean pore radius (mm). According to Dullien (1979), the mean pore radius can be calculated as  $0.4 \cdot d_{50}/2$ . The calculated capillary rise (Table 2) was between 41.6 (for

activated carbon and diatomite) and 159.4 mm (for limestone sand), which corresponds to the content of particles smaller than 0.5 mm.

The values of hydraulic conductivity determined for the reactive materials tested ranged from  $1.19 \cdot 10^{-4}$  m/s to  $2.33 \cdot 10^{-3}$  m/s (Figure 4b). The highest value of this parameter was observed for silica spongolite, a material with the widest range of particle sizes, and the lowest for halloysite. Interestingly, limestone sand was characterized by a higher hydraulic conductivity compared to activated carbon, ZVI, zeolite and halloysite, despite the fact that this material has the highest percentage of fractions smaller than 0.5 mm.

The hydrophobicity tests based on the droplet soaking time allowed characterizing all analyzed materials as hydrophilic materials (Table 2), while according to the hydrophobicity classification presented by Doerr et al. (2000) the materials are included in the class of wettable materials. For all materials tested, the measured time was shorter than 1 second, only for activated carbon it was equal to 1.5 seconds. It is worth mentioning that the tests were performed for the materials dried at 100°C to reflect the least favorable conditions, because dry soils have the strongest hydrophobicity.

### DISCUSSION OF THE TEST RESULTS

On the basis of the test results, the materials were assessed in terms of their potential suitability for use as filling material in the treatment zone enhancing removal processes within infiltration systems. The materials were compared only among each other; in this evaluation they were not compared to other materials that were not characterized in this paper. Therefore, each feature was normalized into the scoring range of 0

**Table 2.** Hydrophobicity and other characteristics determined from particle size distribution

Parameter \ Material	Activated carbon	ZVI	Diatomite	Zeolite	Limestone sand	Silica spongolite	Halloysite
$d_{10}$ (mm)	0.77	0.6	1.12	0.43	0.28	0.60	0.27
$d_{50}$ (mm)	1.84	0.77	1.84	0.70	0.48	1.34	0.59
$d_{90}$ (mm)	1.89	0.90	2.69	0.90	0.66	2.40	0.90
$C_U$	1.90	1.33	1.90	1.74	1.89	2.65	2.37
$C_C$	0.89	0.88	0.67	0.97	0.83	0.67	0.88
Range of particle size (mm)	0.20–2.00	0.40–2.00	0.63–3.15	0.20–1.00	0.20–1.00	0.2–3.15	0.2–1.0
Content of $d < 0.5$ mm (%)	3.0	3.1	0	13	53	4.3	42
Hydrophobicity (s)	1.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Capillary rise $h_c$ (mm)	41.6	99.4	41.6	109.3	159.4	57.1	129.7

to 1. The number of scores (S) for the individual reactive material and particular feature was calculated from the following formula:

$$S = \frac{(a - \min)}{(\max - \min)} \quad (1)$$

where: *a* – parameter value for a given material;  
*min* and *max* – the least and most desirable value of the parameter.

The ranking value (RV) was calculated as the average number of scores for all features. Screening of the tested reactive materials taking into account the analyzed parameters showed activated carbon as the material that best meets the analyzed criteria (Figure 6). Among the mineral materials, most points were assigned to silica spongolite and zeolite.

When analyzing surface structure, it is important to emphasize the large diversity both among all materials and in the group of mineral materials themselves. It is commonly believed that the sorption capacity of materials increases along with the specific surface area, which is also influenced by the pore volume, mainly due to the fact that adsorption is a surface process (Huang et al. 2015, Kumar et al. 2019, Yong and Muligan 2004). This applies to both organic and inorganic substances present in the runoff water. Consequently, it may be supposed that the largest amount of contaminants will be removed via adsorption on activated carbon and, from mineral materials, on halloysite. In addition, the pore dimensions and their arrangement determine the availability of pores and the type of contaminants removed by adsorption, because they act as a “sieve” allowing the molecules with given sizes to “enter” into the material structure (Tran et al. 2017). Kumar et al. (2019) pointed out that the diffusion processes

of contaminants may be affected by pore size as well, influencing at the same time the kinetics of the adsorption processes. For example, the phosphate molecule has a diameter of about 0.48 nm (Tawfik and Viola 2011), the ammonium cation has a diameter of 0.350 nm, copper, the empirical atomic diameters of zinc and nickel are equal to 0.270 nm and the empirical atomic radiuses of lead amount to 0.350 nm (Slater 1964). Taking into account the diameters of the mentioned inorganic contaminants and the dimensions of the pores of reactive materials, it can be assumed that contaminants once adsorbed in micropores can block other contaminants from accessing the pores. According to Huang et al (2015), larger volume of micropores results in greater surface area of the material, but also in lower mass transfer and adsorption rate. It should be noted that for adsorption processes, well-developed micropores are important, while macropores allow contaminants to penetrate deep into the material structure (Kłapyta and Żabiński 2008). It can be concluded that the best potential in terms of contaminant removal via adsorption processes has activated carbon – the material with the best developed surface area of micro- and mesopores, and the lowest – ZVI. In addition, halloysite structures with characteristic nanotubes and a zeolite molecular sieve structure deserve attention. These materials are also characterized by the best developed specific surface and the largest pore volume among the analyzed mineral materials. On the other hand, Kumar et al. (2019) proved that pores of diameters exceeding 10 nm play a crucial role in improving the adsorption kinetics. Thus, the average pore diameter of zeolite, limestone sand, silica spongolite and halloysite may imply good adsorption kinetic characteristics of these materials. When assessing the materials for this feature,

		ZVI	AC	Z	SS	D	H	LS
Number of scores (S)	Specific surface area	0	1	0.042	0	0.037	0.065	0
	Total pore volume	0	1	0.133	0.012	0.080	0.286	0.30
	Average pore size	0.706	0	1	0.609	0.281	0.719	0.698
	pH	0.782	1	0.611	0.753	0	0.447	0.892
	Oxidation-reduction potential	1	0.513	0.493	0.473	0	0.202	0.627
	Cation exchange capacity	0	0.051	1	0.658	0.118	0.091	0.009
	Hydraulic conductivity	0.126	0.194	0	1	0.439	0	0.209
	Capillary raise	0.501	1	0.425	0.868	1	0.252	0
Ranking value (RV)		0.389	<b>0.595</b>	<b>0.463</b>	<b>0.547</b>	0.243	0.258	0.305

Figure 6. Ranking of the reactive materials based on the tested properties

the highest average pore size value (Figure 6) was considered to be the most convenient, which was related to the availability of pores for a larger spectrum of pollutants.

The analysis of crystalline and polycrystalline substances, as well as determination of the phase composition allow predicting the physico-chemical interactions between the solid particles and contaminants present in water. Since carbonate minerals are considered to be good adsorbents of phosphate and heavy metals, and the presence of calcite influences the pH of the solid/water environment (Yong and Muligan 2004), the mineralogical composition of limestone sand and silica spongolite may suggest the dominant role of sorption processes in runoff water treatment. Additionally, kaolinite, halloysite, zeolite and hematite were used as adsorbents of some metal ions (Ahmed et al. 2013, Gruszecka-Kosowska et al. 2017, Inglezakis et al. 2018), while halloysite with induced positive charge was applied as an adsorbent of e.g. orthophosphate, sulfate and nitrate (Matusik 2014). The mineralogical composition closely affects the pH of a solid/water system, which is the most important control of metal partitioning (Yong and Muligan 2004). Considering the contaminants present in the road runoff water, the pH value may influence the treatment processes, especially of heavy metals, but also of ammonium ions. The pH value higher than 7 will result in the conversion of ammonium ions into the form of gaseous ammonia, while heavy metals will precipitate primarily in the form of hydroxides (Pb at  $\text{pH} > 7$ ; Cu at  $\text{pH} > 7.5$ ; Zn at  $\text{pH} > 8.7$ ; Ni at  $\text{pH} > 9.8$ ). It can therefore be expected that in the case of the contact between runoff water containing Pb and Cu with active carbon, ZVI, limestone sand and silica spongolite, precipitation will play a significant role in the process of removing these contaminants, while ammonium ions will be released in a gaseous form to a variable extent. When comparing the materials, it was assumed that higher pH values result in better conditions for the runoff water treatment. However, it should be noted that this assumption is also associated with certain problems, for example ammonia will be released into the pore air and the precipitated heavy metals will be present in forms inaccessible to sorbents. Acidification of the environment resulting from external factors may result in the increased migration of these components in the subsoil.

When choosing a material useful for the removal of contaminants involved in the oxidation-reaction reactions (e.g. nitrates, nitrites, chlorinated hydrocarbons) the ORP should be analyzed. It measures the tendency of a substance to obtain electrons and be reduced (Rajib et al. 2019). The runoff water contains both nitrates and short-lived nitrites, which are considered to be extremely mobile forms of nitrogen in the soil/water environment due to their high solubility and low affinity to the surface of ground particles. In this context, it is likely that ZVI will stimulate the oxidation-reduction processes of these compounds. The properties of the remaining materials do not indicate enhancement of these processes.

One of the processes included in the broadly understood sorption is ion exchange, the measure of which can be the CEC. According to Petersen et al. (1996), the CEC is strongly correlated with the specific surface area. However, no correlation between  $S_{\text{BET}}$  and CEC was observed for the tested materials. Zeolite and silica spongolite are characterized by significant values of this parameter. Due to the negative charge of the zeolite surface (substitution of  $\text{SiO}_4$  by  $\text{AlO}_4^-$ ), it is a commonly used material for removing contaminants from solutions by ion exchange, while the use of silica spongolite is less widespread. The negative charge of silica spongolite, diatomite and halloysite may come from the  $\text{SiO}-\text{H}$  group on the surface, because all these materials contain  $\text{SiO}_2$  in their oxide composition (3.5%, 59.5% and 51.0% respectively). However, the CEC value and  $\text{SiO}_2$  content were not correlated quantitatively. Although this feature is mostly considered as positive, the ion exchange processes can be undesirable in treating the runoff water generated in cold regions. This is related to the potential intermittent release of the previously immobilized contaminants due to de-icing salts, and more specifically the Na, Mg and Ca ions, present in the runoff water.

Theoretically, the best treatment results should be obtained for the fine-grained materials, containing a high proportion of clay and organic parts. Similar relationships have also been observed under laboratory and field conditions, including the studies by Yong and Mulligan (2004) and Kumar et al. (2019). This is primarily due to the positive correlation between the size of the solid particles and their specific surface. On the other hand, considering only the unit volume of the runoff water that can be treated as it flows through a treatment zone filled with reactive

material, the potentially most desirable material would be the one with the highest water transmission. Additionally, in the so-called infiltration systems such as soakaways, the water has to be stored immediately after rainfall and then systematically discharged into the surrounding soil. In this case, the essence is the porosity of the backfill material; therefore, e.g. coarse gravel, pea gravel or 4/40 aggregate material are commonly used for this purpose (Pazwash, 2016). The reactive materials were assessed on the basis of the value of hydraulic conductivity determined under saturated conditions. The materials tested cannot be used as separate materials for filling the storage zone of infiltration systems (e.g. soakaways). Nevertheless, the values of this parameter are greater than the minimum hydraulic conductivity values of soils in the subsoil in the area where soakaways and other infiltration systems are used –  $2.0 \cdot 10^{-6}$  m/s (Schueler 1987, Pazwah 2016). Therefore, the analyzed materials can be used as one of the elements of the systems between the storage zone and the surrounding soils. It must be emphasized that this parameter significantly affects the possibility of using a given material in infiltration systems (e.g. soakaways, infiltration ditches and basins). However, the ability to drain water through the systems that additionally perform the function of runoff water treatment is not the only significant property. It cannot be unequivocally stated that with increase of the value of hydraulic conductivity the suitability of materials for use in treatment systems decreases. However, greater flow rate through the treatment zone potentially shortens the time of contact between the material and the contamination and thus the time of treatment processes. Therefore, the most challenging optimization task faced by the designer is to select a material that is equally sufficiently well-permeable and supporting of the treatment processes.

It should be noted that the hydraulic conductivity of a porous medium to a large extent also depends on its grain-size and particle compaction. According to the calculations performed by Mumford et al. (2013), a decrease in grain-size below 0.5 mm leads to a rapid increase of the capillary rise value ( $h_c$ ). In consequence, coarser materials should be considered for application in permeable treatment zones located in cold regions. This is due to the fact that the water remaining in the system during the winter affects the hydraulic conductivity of the treatment zone

before it is completely melted. Conversely, according to Kumar et al. (2019), particle size may influence the adsorption kinetics; higher values of the kinetic rate constant were observed for materials characterized by smaller particles.

According to the subdivision given by Witun (1987), all materials tested are uniformly grained ( $C_U$  in the range from 1 to 5), while on the basis of  $C_U$  and  $C_C$  reactive materials can be considered as mono-fraction. However, taking into account the criteria set by the filter materials by AWWA (2002), the particle size distribution of the materials is variable, because  $C_U$  is greater than 1.7. The exception is ZVI ( $C_U = 1.33$ ), which meets the criterion for high-density materials ( $C_U < 2.2$ ). At the same time, activated carbon, zero-valent iron, zeolite, and silica spongolite meet the criterion referring to diameter  $d_{10}$ , which should be in the range of 0.35 to 0.65 mm for sand filters, 0.6 to 1.6 for anthracite filters and 0.18 to 0.6 for high-density materials (AWWA 2002). Diameter  $d_{10}$  was smaller for limestone and halloysite and larger for diatomite than the recommended values. From the application point of view of materials used as a filter bed, it is preferable to use the homogeneous materials with coefficient of heterogeneity of  $C_U$  less than 1.7 for the light materials with specific density greater than  $1.4 \text{ Mg/m}^3$  (organic materials such as activated carbon) and the mineral materials with specific density greater than  $2.5 \text{ Mg/m}^3$ , and of  $C_U$  less than 2.2 for the materials with specific density greater than  $3.8 \text{ Mg/m}^3$  (e.g. ZVI) (AWWA 2002). This criterion is only met by zeolite and zero-valent iron.

An important role in the flow of polluted water is also played by the hydrophobicity of porous materials, which is defined as their tendency to repel water molecules from each other. In an unsaturated medium, the flow is the result of gravity and interfacial pressure differences, which depend on the wetting properties, but also on pore geometry (Bachmann et al., 2007). The application of hydrophilic materials is particularly justified when the degree of saturation of the medium changes due to the weather conditions. This results from the fact that in contrast to hydrophobic materials, water flows first through small pores and not through large pores (Wang et al. 2000, Hallet et al. 2011). Conversely, the hydrophobic nature of the materials can 1) induce the development of preferential flow paths, consequently limiting the contact of contaminated waters with reactive materials and reducing the intensity of

the treatment processes taking place (Ritsema and Dekker, 2000), 2) change the soil water dynamics, 3) decrease the infiltration rate (Hallett et al. 2011), and 4) cause the occurrence of fingering (Wang et al. 2000). This feature is important when predicting the water flow through the treatment layer in the first phase of the runoff occurring just after a period of drought. The material hydrophobicity tests did not indicate a potential problem with the infiltration of runoff water after drying of the materials, e.g. during a rainless period of high temperatures. All materials are hydrophilic, only activated carbon showed a longer droplet penetration time compared to other materials. This may be due to the presence of both hydrophilic and hydrophobic sites on the surface of activated carbon (Groszek and Partyka, 1993). It should be emphasized that the hydrophobicity of the materials used to build systems based on the filtration of the runoff water can be increased due to their long-term contact with oil derivatives, which are apolar particles. Given the above, it can be concluded that the hydrophilic nature of all analyzed materials will not negatively affect the water flow through the newly built-in layer of reactive material.

To sum up, it should be stated that the reactive materials tested can be assessed as good or moderately good materials in terms of their application in the treatment zones of the runoff water from urbanized areas (more specifically from road infrastructure). However, despite their earlier use in water and wastewater treatment, further research should take into account the influence of external factors (e.g. temperature, geochemistry, large loads of dissolved salt) on the stability of the treatment processes.

## CONCLUSIONS

The assessment of the suitability of reactive materials for their application in the runoff water treatment technologies should be carried out on the basis of both the properties of the materials and the contaminants to be treated. Only the knowledge of these two characteristics allows for drawing the conclusions about the potential interactions between the contaminants and solid particles. Firstly, the conducted analyses allow assuming that due to the most extensive specific surface area and developed surface area of micro- and mesopores, the largest amount of contaminants

may be removed via adsorption on activated carbon and halloysite. The average pore diameter of zeolite, limestone sand, silica spongolite and halloysite may imply good adsorption kinetic characteristics of these materials. However, after being adsorbed in micropores, contaminants may block other contaminants from accessing the pores of all reactive materials tested. Secondly, the high values of pH of active carbon, ZVI, limestone sand and silica spongolite may suggest the dominant role of heavy metal precipitation in the runoff water treatment. Additionally, ammonium ions will be released in a gaseous form of ammonia under alkaline conditions. Thirdly, the values of hydraulic conductivity allow considering the analyzed materials as fillers of treatment zones enhancing the removal of contaminants from the runoff water in infiltration systems. Eventually, the assessment of the application potential of reactive materials taking into account their physicochemical and hydraulic parameters indicated activated carbon, together with silica spongolite and zeolite (among mineral materials), as the materials that best meet the analyzed criteria.

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