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The Testing of Standard and Recyclable Filter Media to Eliminate Hydrogen Sulphide from Sewerage Systems

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Abstract: This article focuses on the subject of odours forming in sewage transfer chambers with displacement inlets, as well as the odours in their vicinity. It further covers the locations of odour formation, factors influencing the formation of hydrogen sulphide in wastewater, methods of removing hydrogen sulphide from wastewater, and laboratory testing of filtration media efficacy at various concentration levels of H_2S. The laboratory testing of filtration media efficacy is performed for products normally used by sewerage system operators guaranteeing the elimination of hydrogen sulphide (activated carbon, natural minerals and gels), recyclable materials (paper) and secondary raw materials in the field of waste management (biochar—the final product of microwave pyrolysis). Odour generated by sewerage systems is a secondary issue faced by all sewerage system operators, who sustain considerable expense in corrective measures to address this problem. The most economical and widespread measure used by those operators is hydrogen sulphide removal by filtration (filtration materials). Filtration media are installed in special cartridges under sewage covers in locations where the irritating odour is formed. These filtration cartridges, designed solely to eliminate odour from the surroundings, show various degrees of efficacy in removing H_2S.

Keywords: hydrogen sulphide; odour removal; filtration media efficacy; sorption capacity

1. Introduction

Odour is one of the organoleptic properties of wastewater, which differ in terms of smell sensitivity. The sewerage operator should prevent the formation of odours and try to emit as few odour components into the air as possible. The primary objective is to prevent the formation of odours, mainly by controlling and managing processes at the producer level, as well as in the sewerage system and wastewater treatment plant [1]. However, odour cannot often be reduced at the point of origin and it is, therefore, necessary to apply a secondary solution to prevent the spread of odour and its resulting hazardous substances.

As a result of organic matter degradation by microorganisms under anaerobic conditions, odours are already formed during wastewater flow in the sewerage system. Another source of odorous substances is industrial wastewater connected to the public sewerage system. Wastewater components participating in the formation of odour [2,3] include sulphide (hydrogen sulphide), ammonia, organic sulphur compounds, thiols (e.g., mercaptans), amines (indole and skatole) and other organic compounds.

The characteristic conditions for the formation of odour in the sewerage network can be defined as:

- in sewerage networks and house drains under adverse technical conditions;
- in transfer manholes with delivery pipe inlets;
- in long pressure pipes;
- in discharges of special industrial wastewater;
- in wastewater reuse by consumers and the resulting minimal flow rates in sewers;
- in sludge storage and sludge treatment facilities (sediments);
- improper operation and maintenance of both sewerage and facilities.

Elimination of odour from sewerage systems should be a high priority of operators. Odour causes nuisance to inhabitants living in the vicinity of the sewerage systems and has a direct impact on the service life of those sewers and machinery installed in sewerage facilities. In this case, the operator should perform a sensitivity analysis of the sewerage system and facilities, based on various combinations of variables, in order to assess the reliability of pipes and facilities using a software developed model [4,5].

European Union law defines "odour quality" in Directive 2008/50/EC of the European Parliament and of the Council on ambient air quality and cleaner air for Europe [6] for Europe and Directive 2010/75/EU of the European Parliament and of the Council on Industrial Emissions, Integrated Pollution Prevention and Control [7].

Sulphates (SO_4^{2-}) are converted by bacteria in municipal wastewater and through their metabolism into hydrogen sulphide. This process occurs predominantly in biofilms and sediments under anaerobic conditions in a submerged part of the sewer. The major reactions involving sulphur compounds in sewage are:

1. Reduction of sulphate to sulphide by sulphur-reducing bacteria.
2. Decomposition of amino acids containing sulphur.
3. Methylation of methyl mercaptan (CH_3SH) by H_2S [3,8].
4. Dimethyl sulphide (DMS) generation via oxidation of CH_3SH [9].

Hydrogen sulphide easily escapes from water, predominantly in areas of turbulent flows where water is spread into the surrounding air. Volatile hydrogen sulphide is heavier than the air and it accumulates in the free space inside the sewerage where it is slowly carried by the stream of wastewater in gravity sewers [10,11].

The main factors influencing the formation of odour in the sewerage are:

1. Sewage composition: there is a significant influence of sulphide and sulphate concentrations in wastewater and special industrial service water [12]. Oxidation-reduction potential with values suited to anaerobic conditions: −50 mV. Temperature: biological oxygen demand increases with rising temperatures and anaerobic conditions are established in the sewerage system [13]. pH value: in more alkaline water there is a lower risk of hydrogen sulphide formation. Oxygen concentration: where values below 0.5 mg/L result in anaerobic conditions.
2. Hydraulic factors: residence time, as longer residence times beyond 8 h result in anaerobic conditions in the sewerage system [12]. Poor technical design of the sewerage, where over-sizing results in low flow rates in the sewerage system, promoting sedimentation and the creation of an anaerobic environment. Velocity gradient, as a high velocity gradient causes considerable release of hydrogen sulphide into the air. Sediments and biofilm, where organic substrate is hydrolysed in anaerobic sediments along with fermentation, sulphate reduction and methane production [14].
3. Sewerage facilities and pumping stations, where long switching intervals of wastewater pumping result in an anaerobic environment. Pressurized sewers, causing long retention times in the pipeline and vacuum stations missing biofilters for exhaust air treatment.

Odour removal technologies can be divided into primary and secondary. The primary activity should be to prevent odour formation through controlled sewerage operations. In many cases, the operation cannot be controlled to avoid such formations. Thus, odour removal is a secondary activity and can be ensured either directly from wastewater or from the air. These activities cannot protect concrete pipelines against biogenic sulphuric corrosion. The hydrogen sulphide formed escapes through sewerage manholes to the surroundings and causes nuisance to the inhabitants, mostly in the summer months.

Methods of removing odour from wastewater consist of chemical dosing into wastewater, which limits the formation of odour compounds. Such chemical dosing is carried out and recommended to be performed directly at the sewerage pumping stations. Methods used for the removal of odour from wasterwater are listed in Table 1.

Table 1. Methods of removing odour from wastewater.

Iron salts precipitation	Iron can restrict the formation of sulphide in its divalent and trivalent forms. Divalent iron and sulphide form a black precipitate of ferrous sulphide. Trivalent iron can cause sulphate to be eliminated by producing elemental sulphur and oxidising to divalent iron. These iron salts used include ferrous chloride ($FeCl_2$), ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) and iron chloride sulphate ($FeClSO_4$) [15].
Chlorination	Chlorine is dosed into wastewater as a solution of gas that removes sulphide ions. The efficiency of sulphide reduction is limited due to the ability of chlorine to oxidise with organic and inorganic compounds. Adverse substances formed during the reaction of chlorine and certain organic substances with wastewater are trihalomethanes [16].
Oxidation by hydrogen peroxide	Hydrogen peroxide can oxidise sulphide to produce water and oxygen. In addition, by producing oxygen, hydrogen peroxide can contribute to maintaining aerobic conditions in wastewater and achieve high removal rates [17].
Oxidation using potassium permanganate	Potassium permanganate (KMnO4) is a strong agent that is capable of oxidising sulphide to sulphate. Typically, potassium permanganate is distributed in the dry state and it is therefore necessary to obtain an aqueous solution before application [18].
Biological oxidation of sulphide	The sulphide inhibition process also eliminates two types of bacteria—*Thiomicrospira denitrificans* and *Thiobaciluus denitrificans*. In the presence of nitrates, these bacteria are capable of oxidising sulphides and sulphur. Necessary electrons are taken from nitrates, which results in their reduction [19].
Restriction of anaerobic conditions using nitrate solution	Nitrate addition can establish anoxic conditions in wastewater. Nitrates are more easily reducible than sulphate in this environment, hereby reducing sulphide formation.
Compressed air or pure oxygen	Wastewater aeration is most often applied in pressure pipes or wet pits. Pure oxygen is five times more concentrated than oxygen contained in the air and, therefore, it is possible to achieve higher dissolved oxygen values in wastewater using oxygen 5 to 7 $mg \cdot L^{-1}$ than using air 3 to 5 $mg \cdot L^{-1}$.

Secondary methods of removing odour from the air consist in the installation of an auxiliary system which, by means of physical, biological and chemical processes, captures hydrogen sulphide escaping into the environment. Methods used to eliminate odour from air are listed in Table 2.

Table 2. Methods of removing odour from the air.

Air scrubber, oxidation and absorption	This technology can be used to treat practically all water-soluble contaminants. Liquid in the washer is sprinkled and creates artificial fog. The harmful substances are entrapped by the fog and dissolved from their gaseous phase into aqueous chemical solutions. The reaction mechanism is purely chemical and stable, resisting changes of input substances and external conditions [20].
Bio-air scrubbers	The bio-scrubber is fitted with an artificial carrier designed to have the largest possible surface area. Biofilm is then formed on the surface by sprinkled medium and substances separated from the air. There are two processes taking place in the biofilm, both physical and biochemical. As part of the physical process, gas molecules enter the sprinkled liquid and in the biochemical process the pollution is directly degraded in the liquid with the help of microorganisms [21,22].
Biological filters	This principle is similar to the bio-scrubber. The difference is that, instead of the biofilm medium, the filter medium is firm and the odorous substances are absorbed and degraded by microbiological organisms.
Biofilters with forced dry matter extraction	This biological filter technology can be used to treat various biodegradable water-soluble contaminants. Harmful substances from the air are dissolved in the filter from the gaseous to aqueous phase on the surface of an organic medium. For example, peat, tree bark, modified root and coconut fibres, as well as compost are used. Odour molecules are then degraded by the bacterial population in this medium [23].
Biofilters without forced dry matter extraction	Due to the absence of a ventilator and without the need for power supply for the ventilator, this type of filter can be directly fitted into the sewer manhole under the cover. The filter medium and its fraction must be selected so that the air can freely escape from the sewer without causing a significant pressure loss in the air flow [24].
Adsorption on filter material	When a filter material is used, the air flow passes through an adsorbent layer. The odour-causing compounds are attracted to the surface of the adsorbent. This is the simplest of the aforementioned odour-removal technologies. There is no need for any chemicals to be dosed into the system and there is no need to control biological processes that might be disturbed.
Photooxidation, ozonisation, ionization	To remove harmful substances from the air, ozone and hydroxyl ions are also used that are supplied into the air using strong electric discharges or short-wave ultraviolet (UV) radiation. This technology is preceded by a particulate filter so as not to damage UV lamps and electrodes.
Neutralization, compensation and masking	These methods only mask odours and the harmful substances lose their noticeable organoleptic properties. However, individuals are still in contact with dangerous substances and this makes it all the more dangerous because the odour loses its warning property. Essential oils and various natural and synthetic substances are used for this purpose. There are no chemical processes in contact with the air.
Fresh air dilution	Dilution of odorous substances is important in those cases where the operator wants to protect the pipeline from biogenic sulphide corrosion and it is possible to vent out large volumes of foul-smelling air into rural areas. The concentration of odorous substances in sewerage is significantly reduced by using a ventilator located in the pipeline.

The application of filtration media under the covers of the sewage chambers is the most widespread measure taken by operators of sewerage systems. Currently, the most common application uses standard filtration media on the basis of organic carbon, placed into special cartridges. Products offering filtration media used for sewage chambers worldwide are very widely used, with varied guaranteed effectiveness. So far, an overall independent effectiveness comparison of filtration media used has not been carried out.

2. Materials and Methods

Recycled materials from garbage management were also included among standard filtration media, such as recyclable paper and biochar (a product of microwave pyrolysis). The manipulation with and use of recycled material is in accordance with the strategic concept of a circular economy.

2.1. Parameters of Laboratory Measurement

Filtration media testing was carried out in a filtration column with a reaction tank for the production of hydrogen sulphide. Hydrogen sulphide was produced using powdered ferric sulphide FeS in a reaction vessel, with a dosing of hydrochloric acid HCl diluted with distilled water (see Equation (1)) and using a peristaltic pump into the reaction chamber.

$$FeS + 2HCl \rightarrow H_2S + FeCl_2 \quad (1)$$

Molar mass of individual compounds Mr (FeS) = 87.834 g·mol^{-1}, Mr (H_2S) = 34 g·mol^{-1}. Amount of substance FeS = 0.0114 mol with a theoretical volume of 0.255 L.

Constant flow monitoring was provided by manometer and anemometer detectors with a control system. Measurement of hydrogen sulphide concentration at the inlet and outlet of the filter column was performed by a detector with a datalogger, manufactured by OdaLog Logger L2, with the following parameters:

- input detector: LL-H_2S-1000, declared measuring range of 0–1000 ppm with a resolution of 0.5 ppm and detector accuracy of 0.5%,
- output detector: LL-H_2S-200, declared measuring range of 0–200 ppm with a resolution of 0.1 ppm and detector accuracy of 1%. Recorded measuring range of 350 ppm with a resolution of 0.1 ppm.

All the tested filtration media had the same boundary conditions set for laboratory measurements, which were calculated or verified during operation. The filtration media efficacy testing parameters for hydrogen sulphide removal filters are:

- volume of one tested filtration medium: 0.5 L;
- maximum concentration of hydrogen sulphide at the inlet to the filtration unit: 300 ppm;
- maximum duration of one test: 30 min;
- hydrochloric acid concentration—HCl: 35%;
- dilution ratio with distilled water: 1:8;
- FeS volume: 1 gram;
- air flow rate set by anemometer: 3 L·min^{-1}.

Laboratory conditions for measuring the efficiency of filtration media:

- all filtration products were stored in a dry laboratory environment;
- testing was performed at a constant temperature of 20 °C;
- air humidity was maintained at 55%;
- atmospheric pressure in the room equalled 1013.25 hPa;
- and constant temperature of the filtration media was 20 °C.

The laboratory space was aired out after each measurement, along with a control measurement for H_2S neutral odour and calibration of both H_2S detectors. The testing of each filtration medium took place on three occasions to ensure sufficient measured data for statistical evaluation.

Before the laboratory tests, the anemometer was used to determine the actual airflow values in the sewerage. The air flow set through the filter column in the laboratory was selected with a 100% reserve.

2.2. Filtration Media

The filter media tested are divided into three basic groups according to structure, these being pelletized materials, granulates and gels—see Tables 3–5.

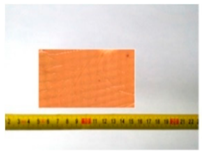
Table 3. Selected filter medium pelletized.

Filtration Medium	Description	Manufacturer	Structure	Photo Documentation
Activated carbon extruded Identification: AddSorb VA3	Intended for gaseous phase based on graphite plates with a large internal surface.	Jacobi Carbons Parent Company [25] Made in: Japan	Bulk material Granulometry 4–8 mm	
Biochar I	Product of spruce wood microwave pyrolysis unit.	Bionic E & M, s.r.o. Brno University of Technology, AdMaS Center [26] Made in: Czech Republic	Bulk material Granulometry 2–10 mm	
Biochar II	Product of sewage sludge microwave pyrolysis unit.			
Product Identification: Biofilter Rehau	Recyclable old paper without black ink.	Rehau company [27] Made in: Switzerland	Bulk material Granulometry 5–30 mm	

Table 4. Selected filter medium granulates.

Filtration Medium	Description	Manufacturer	Structure	Photo Documentation
Clayey granulate Identification: Granulit Air	Strong deodorizing agent. Porous granulate, excellent decomposition of organic substances.	Biothys asia co., Ltd. [28] Made in: Korea	Bulk material Granulometry 4–8 mm	
Natural mineral Zeolite	Alkali metal aluminosilicate crystalline and alkaline earth metals.	Subio, s.r.o. [29] Made in: Czech Republic	Bulk material Granulometry 2.5–5 mm	
Natural mineral Identification: Grena GV Vermicularis	Mineral-phyllosilicates. This serves as a carrier layer for gels that soak into GV and do not cause their loss.	Grena, a.s. [30] Made in: Czech Republic	Bulk material Granulometry 0–5 mm	

Table 5. Selected filter medium gels.

Filtration Medium	Description	Manufacturer	Structure	Photo Documentation
Milky white gel Identification: Ecosorb 505	Mixture of natural essential oils and food grade emulsifiers.	OMI Industries, co. [31] Made in: USA, Illinois	Gel form	
Milky white gel Identification: Ona Gel Liquid	Mixture of hydrocarbons of plant origin and chemical compounds for odour neutralization.	Odorchem Manufacturing co. [32] Made in: Canada	Gel balls	
Blue gel Identification: Bad Air Sponge	Gel containing activated carbon, wetting and neutralizing agents.	Mateson Chemical Corporation [33] Made in: USA, Philadelphia	Semi-solid gel	
Orange gel Identification: Gelactiv Suspension	Gel plate containing active substances in the neutralization process.	Biothys GmBH [34] Made in: Germany	Gel plate	

The recyclable material is the cellulosic biofilter Rehau containing nutrients. The secondary raw material is biochar, the product of the microwave pyrolysis process. The pyrolysis unit is located in the laboratories of AdMaS Research Center, Technical University in Brno, Faculty of Civil Engineering.

Spruce wood was used for the microwave pyrolysis (filtration medium Biochar I in Table 1) and sludge from the municipal wastewater treatment plant in Karlovy Vary, Czech Republic (filtration medium Biochar II in Table 1) with a design capacity of 80,000 PE.

Biochar I is a pyrolysis product produced without admixtures. Biochar II is a pyrolysis product from sewage sludge with an organic dry matter content of 55% and a zeolite admixture at a weight concentration of 1%. The biochar yield from sewage sludge is currently the subject of research at the Brno University of Technology, AdMaS. Without admixtures, the sewage sludge biochar yield contains a small amount of organic matter (up to 23%) and liquid (up to 10%). Biochar II contains organic matter thermogravimetrically 40.3%, Total organic carbon (TOC) biochar 29.3%, biochar yield 58.9%, liquid yield 18.2% and gas yield 22.9%.

A Grena GV Vermicularis natural mineral test was carried out in combination with Ona Gel Liquid and Ecosorb 505 milk gels. The ratio between the Grena GV Vermicularis filtration material and the Ona Gel and Ecosorb 505 gels was experimentally established at 1:1. The gel producers do not recommend any optimum ratio with other filtration materials.

The basic composition of all filtration media, i.e., the main and secondary components of the media are listed by the manufacturer in the product data sheets and have not been tested by the laboratory.

No material inoculation was performed and there was no conditioning, stability of the material during the test, material compaction, and water retention in the material. The damping capacity of the filtration media was not evaluated.

3. Results

The evaluation of overall efficiency of filtration media used an original multi-criteria analytical method—see Table 6. Among the evaluation criteria were: effectiveness of the filtration medium, sorption capacity of the filtration medium, preparation of the filtration medium prior to the experiment into the filtration column and the odour impression.

The service life of the filtration media is set by each manufacturer in the product data sheets.

The preparation of the filtration material is an indicator defining a collection of works prior to testing of the filtration material. Preparation works included manipulation of the material, its treatment prior to filling, and emptying the test cartridge.

Residual odour perception was evaluated at the end of laboratory testing for all filtration materials and is based on the sensory sensitivity of an experienced laboratory worker.

Purchase price of the filtration material was not included in the evaluation criteria due to varied stock levels of the suppliers, various specific costs regarding their purchase, our own production costs and varying costs of material delivery.

Mathematically, the evaluation of the overall efficiency of the material can be expressed using Equation (2).

$$u^i = \sum_{j=1}^{n} v_j \cdot C_j^i \tag{2}$$

where: i—1, 2, ... p,

u^i—general assessment of i-media;

v_j—rate of importance of j-criterion;

$C_j{}^i$—sub-assessment of i-media based on j-criterion;

n—number of criteria;

p—number of media.

Table 6. Proposed evaluation criteria of filtration media.

Group of Criteria—Indicator Weight	**Category Description Criterion Weight**	**Classification at the Level**			
		CI	**CII**	**CIII**	**CIV**
		0.1	**0.15**	**0.25**	**0.5**
Category C1—0.70	Filtration medium effectiveness	>90%	70–90%	70–50%	<50%
Category C2—0.15	Filtration medium sorption capacity	>12 months	6–12 months	3–6 months	<3 months
Category C3—0.10	Filtration medium preparation	Excellent	Good	Sufficient	Insufficient
Category C4—0.05	Residual odour perception	None	Mild	Strong	Extreme

The final assessment values "u^i" are dimensionless figures in an interval <0.1–0.5>. Sufficient filtration media are recommended due to their resulting values in the interval of <0.1–0.25>, less suitable values in the interval of <0.25–0.40> and unsuitable in the interval of <0.4–0.5>. We recommend suitable and less suitable filtration media for direct application under the sewage covers in sewerage systems. The minimum required effectiveness of the filtration material should be larger than 60% (Category CII).

The measured results shown in Table 7 include detector deviation at the inlet and outlet of the filtration column.

Table 7. Recommendations for applications of filtration media in sewerage systems.

Final Order	Tested Medium	Filtration Medium Effectiveness			Category				General Assessment Media
		Min.	Max.	Average	C1	C2	C3	C4	
1.	Activated Coal AddSorb VA3	98.0	99.5	98.9	CI	CI	CI	CI	0.100
2.	Biochar I	85.1	73.1	78.4	CII	CII	CI	CI	0.138
3.	Biofilm Rehau	52.1	65.1	59.6	CIII	CI	CI	CII	0.213
4.	Gelactiv Suspension	51.2	70.2	64.1	CIII	CII	CIV	CII	0.255
5.	Biochar II	31.6	42.1	37.0	CIV	CII	CI	CII	0.388
6.	Grena GV Vermicularis and Ecosorb 505	1.4	4.1	2.7	CIV	CII	CII	CIII	0.410
7.	Zeolite	6.8	9.3	8.4	CIV	CI	CI	CIV	0.440
8.	Grena GV Vermicularis and Ona Gel Liquid	2.8	11.5	6.9	CIV	CII	CII	CIV	0.448
9.	Granulit Air	22.6	25.2	24.1	CIV	CIV	CIV	CIII	0.463
10.	Bad Air Sponge	9.5	5.5	7.8	CIV	CIV	CIV	CIV	0.500

The winners among the tested filtration media are pelletized materials that have organic carbon as their basic component. The measured values show one common indicator, i.e., decreasing efficiency of filtration media with increasing H_2S concentrations (with the exception of Rehau Biofilm).

Activated Coal AddSorb VA3 shows the highest achieved average efficiency at 98.9%, high sorption capacity over 12 months, and is easy to prepare and handle.

Recycled materials Biochar I and Rehau Biofilm achieved surprising results. Biochar I, a product of microwave pyrolysis, produced from fir wood and containing 100% organic matter, has a very good average efficiency of 78.4%. Rehau Biofilm, a product made from recycled paper, was the only medium whose efficiency increases with the increasing concentrations of H_2S. This product is a combination of a filtration granulate with active substances that microbiologically degrade hydrogen sulphide and transform it into air of a neutral odour. It can be assumed for the relevant product that with higher humidity of the environment and biofilter inoculation, the filtration material will show increased hydrogen sulphide removal efficiency.

Granulated filtration materials show very low efficiency of H_2S removal, equal in terms of units. Their advantage is in easy manipulation and guaranteed good sorption capacity. The main component of zeolite is a clay-silicate mineral and the main component of Grena GV Vermicularis is a phyllosilicate. We can state with regard to their low efficiency in removing H_2S that granulated materials are not suitable as a product for removing H_2S from sewerage systems. The use of separate granulates is preferred as suitable substrates for plants, nutrient management, as e filtration materials for aquariums and ponds, and to prevent algae formation.

Laboratory measurements, graphically evaluated in Figure 1, illustrate that the best base component in the filtration media is organic carbon.

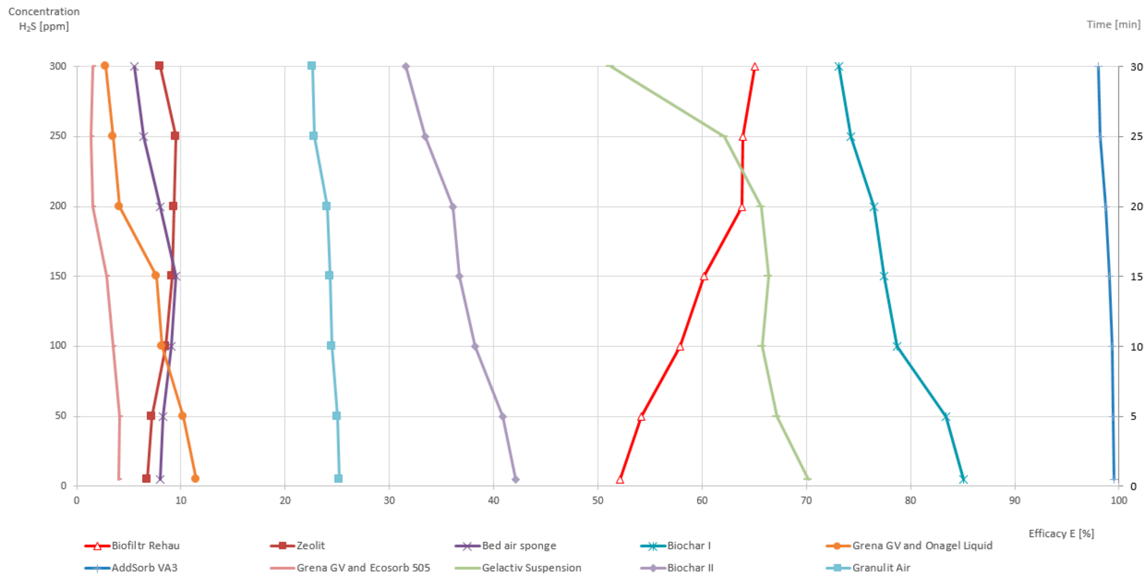


Figure 1. Efficacy of filtration materials.

Filtration medium gels, along with granules, show a removal efficiency of H_2S up to 10% and they have their own smell. Due to the low efficiency of H_2S removal, after the completion of the experiment, the odour impression above the filtration media was very strong. The preparation of the gel is complicated and time-consuming. The gel is supplied in an unsuitable consistency requiring treatment and adjustment to the size of the filtration cartridge. The main components of Grena GV Vermicularis are an emulsifier, an etheric oil and phyllosilicate (Ecosorb 505) or terpenes (Ona Gel Liquid). The main component of Bad Air Sponge is a neutralizing agent with a sorption capacity of 1.5–3 months. The manufacturer recommends the use of gel with granulates to accomodate reduction pressure losses and to potentially aerate the medium. Gels are, according to manufacturers, used to remove H_2S from the air as well as in various environments. The tests proved simple odour masking effects. As regards practical use, masking is very dangerous as human senses do not sense the odour of the original substance and the human body is therefore exposed to hydrogen sulphide for far longer. Granulates and gels are intended for a different area of use than removing H_2S odour—they can absorb moisture and mask odours. However, they are not at all suited for eliminating hydrogen sulphide.

The Gelactiv Suspension gel sheet achieved surprising results as the third highest efficiency of H_2S removal, reaching 64.1%. Its main components are aldehydes and polymeric gel with active substance sorption capacity of 3–6 months. This is a material that neutralized odour with very good results that prioritise the product for direct application.

4. Discussion

Sulphide concentration of around 0.5 ppm already registers in the respiratory system. Operators of sewerage system use various filtration media to eliminate H_2S.

The application of filtration media under sewer covers is the simplest and most widespread measure for the sewerage systems entailing low capital and operating expenditures (capex and opex). This article's innovation is based on an independent comparison of readily available filtration media (pelletized, granulated and gels) and recycled materials (biochar and cellulose paper). The filtration materials were categorized as suitable, less suitable and unsuitable for direct application, using a multi-criteria analytical method stipulating weights of evaluation indicators.

Among the suitable filtration materials were Activated Coal AddSorb VA3, Biochar I (from fir wood) and Biofilm Rehau (cellulose paper). We recommend using these materials under the sewer covers in sewerage systems. We found the Gelactiv Suspension gel sheet and Biochar II (from treatment-plant sludge) less suitable. Grena GV Vermicularis and Ecosorb 505, Zeolite, One Gel Liquid, Granulit Air and Bad Air Sponge were categorized as unsuitable materials.

In general, we conclude that pelletized products on the basis of organic carbon are suitable filtration materials. The sulphide removal is very good at over 70%, the preparation of the filtration material is excellent, and both during and after testing, the filtration medium is without a noticeable odour.

Recycled materials and secondary waste materials are a new group of materials and resources replacing strategic raw materials. In 2014, the EU adopted a strategic concept that aims to implement a so-called "circular economy". The aim is to minimize the volume of materials leaving the economic cycle. In the circular economy, secondary recyclable products have an economic and environmental potential. The current market offers very few recyclable products.

The research and development of new technologies for the production of filtration materials from recyclable and secondary waste materials should be continued along these lines. We are currently researching the uses of secondary waste in the laboratories of AdMaS Research Center, Technical University in Brno, Faculty of Civil Engineering. A pilot unit of microwave pyrolysis tests various combinations of recyclable or waste materials. The result of the thermic microwave degradation of a "mix" of biodegradable waste is a product named biochar. Biochar has a very specific surface—hundreds of square meters per gram, a large sorption capacity and a wide application in practice, including active filtration material, fertilizer, silage agent, fodder supplement, soil decontamination, soil remediation, air humidity regulation and more.

Among the newly tested filtration materials are recycled paper, plastics and organic materials provided by sludge from waste water treatment plants and drinking water treatment plants. Recyclable paper has very good potential, as its fibres are shortened during repeated treatment (known as downcycling). The pelletization of recycled paper enables its repeated use. Currently, newspaper printer paper is being used, although other types of paper are not yet being tested (such as multi-layer Tetrapacks).

Plastics form a significant group of recyclable materials that are not yet used in the area of filtration materials applicable for sewerage systems. Among the potentially usable waste types are polyethylene terephthalate (PET) bottles, polyvinyl chloride (PVC) waste, tyres and more. There is currently no product on the market that would include this group of waste materials.

We always recommend combining recyclable materials such as paper and plastic with an organic material (biofilter, compost and other) or refreshing them with active compounds that increase the overall efficiency of sulphide removal. Recyclable biodegradable waste and secondary waste materials are the future of filtration materials used for the removal of hydrogen sulphide in sewerage chambers.

5. Conclusions

Prior to application of the filtration medium, the operator of the sewerage system must know the concentrations of H_2S reached in the problematic location. The measured sulphide concentrations can occasionally reach up to 500 ppm in a sewerage system (at an air temperature of 20 °C where, at the atmospheric pressure of 101.3 kPa, the dependence is 1 ppm = 1.4 $mg \cdot m^{-3}$).

When applying the filtration medium, the operator aims to achieve the longest possible service life, meaning a decrease of H_2S concentration values and increase in sorption capacity. The service life of the filtration media is affected by temperature, ambient air flow rate, duration of the extreme concentrations of hydrogen sulphide and technical measures taken by the operator in the sewerage system. These technical measures applied in the locality where the odour occurs most often include, the sewerage discharge in the transfer manhole below the wastewater level in the sewerage system, a suction pipeline leading out of the manhole set-up of switching levels in the pumping stations, additional aeration in the sewers, and other measures.

A frequent measure taken by the operator is the replacement of perforated sewer manhole covers with solid covers. Replacement of sewer covers is a measure that only moves the hydrogen sulphide odour along the length of the sewer and with possible consequences of biogenic sulphide corrosion. Sealing the sewer covers by the operator is a technical measure which contradicts standard ČSN EN 752 "Drain and sewer systems outside buildings". The standard requires that gravity sewers and house drains must be sufficiently ventilated into the air while ensuring free passage of air throughout the system [35]. For the application of the filtration material, it is necessary to take into account the ratio between the efficiency and cost of the filtration material, the possibility of material regeneration, sorption capacity, harmlessness and the material handling itself.

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References

1. Gil, K.; Shin, G.; Im, J. Investigation of odor release from combined sewer. *J. Korean Soc. Hazard Mitig.* **2010**, *10*, 185–191.
2. ČSN EN 12255-9. *Wastewater Treatment Plants—Part 9: Odour Control and Ventilation*; Czech Office for Standards, Metrology and Testing: Praha, Czech Republic, 2003.
3. Pandey, S.K.; Kim, K.; Tang, K. A review of sensor-based methods for monitoring hydrogen sulfide. *Trends Anal. Chem.* **2012**, *32*, 87–99. [CrossRef]
4. Kanakoudis, V.; Tsitsifli, S. Reliability assessment & data classification using discriminant functions & factor analysis. In Proceedings of the 4th IWA Specialized International Conference on Water Loss, Bucharest, Romania, 23–16 September 2007; pp. 836–845. Available online: https://scholar.google.ca/scholar?oi=bibs&cluster=14412914019176863058&btnI=1&hl=en (accessed on 13 March 2016).
5. Zeleňáková, M.; Vido, J.; Portela, M.M.; Purcz, P.; Blišťán, P.; Hlavatá, H.; Hluštík, P. Precipitation Trends over Slovakia in the Period 1981–2013. *Water* **2017**, *9*, 922. [CrossRef]
6. European Environment Agency. Council 2008/50/EC. *On Ambient Air Quality and Cleaner Air for Europe*. Directive 2008/50/EC of the European Parliament and of the Council. 2008. Available online: http://data.europa.eu/eli/dir/2008/50/oj (accessed on 14 March 2018).
7. European Parliament. Council 2010/75/EU. *On Industrial Emissions (Integrated Pollution Prevention and Control)*. Directive 2010/75/EU of the European Parliament and the Council. 2010. Available online: http://data.europa.eu/eli/dir/2010/75/oj (accessed on 14 March 2018).
8. Lomans, B.P.; Pol, A.; Camp, H.J.M. Microbial cycling of volatile organic sulfur compounds. *Cell. Mol. Life Sci.* **2002**, *59*, 575–588. [CrossRef] [PubMed]
9. Yarosz, D.P.; Chen, Y.; Murthy, S. Mechanisms of volatile sulfur compounds and odor production in digested biosolids. In Proceedings of the Water Environment Federation, Baltimore, MD, USA, 19–22 February 2013.
10. Zhang, L.; Schryver, P.; Gussume, B.; Muynck, W.; Boon, N.; Vestraete, W. Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: A review. *Water Res.* **2008**, *42*, 1–12. [CrossRef] [PubMed]
11. Dobrynkin, N.M.; Batygina, M.V.; Noskov, A.S. Water depollution and the odor control by wet air catalytic oxidation of ammonia, sulfides, and mercaptans of industrial wastewater. *Chem. Eng. Trans.* **2010**, *23*, 339–344.
12. ČSN EN 1671. *Pressure Sewerage Systems Outside Buildings*; Czech Office for Standards, Metrology and Testing: Praha, Czech Republic, 1998.
13. Sekyiamah, K.; Kim, H.; McConnell, L.L.; Torrents, A.; Ramirez, M. Identification of seasonal variations in volatile sulfur compound formation and release from secondary treatment system at a large wastewater treatment plant. *Water Environ. Res.* **2008**, *80*, 2261–2267. [CrossRef] [PubMed]

14. Ray, S.; Kim, K.; Yoon, H. Effect of incineration on the removal of key offensive odorants released from a Landfill Leachate Treatment Station (LLTS). *Chemosphere* **2012**, *87*, 557–565. [CrossRef] [PubMed]
15. Cipriani, M.; Schiavi, R.; Santos, F. *Odour Control: A Successful Experience in Sorocaba City—Brazil*; IWA Publishing: London, UK, 2018. [CrossRef]
16. Vilmain, J.B.; Courousse, V. Kinetic study of hydrogen sulfide absorption in aqueous chlorine solution. *Chem. Eng. Res. Des.* **2014**, *92*, 191–204. [CrossRef]
17. Cuevasanta, E.; Carballal, S.; Zeida, A.; Alvarez, B. Insights into the mechanism of the reaction between Hydrogen sulfide and peroxynitrite. *Free Radic. Biol. Med.* **2014**, *80*, 93–100. [CrossRef] [PubMed]
18. Willey, B.F.; Jennings, H.; Muroski, F. *Removal of Hydrogen Sulfide with Potassium Permanganate*; American Water Works Association: Denver, CO, USA, 1964; Available online: http://www.jstor.org/stable/41264210 (accessed on 12 March 2018).
19. Zhang, D.; Du, J.; Tang, C.; Huang, Y.; Jin, H. H_2S-Induced Sulfhydration: Biological Function and Detection Methodology. *Front. Pharmacol.* **2017**, *8*, 608. [CrossRef] [PubMed]
20. Chou, S.J. *Hydrogen Sulfide: Human Health Aspects*; World Health Organization: Geneva, Switzerland, 2003; ISBN 9241530537.
21. Aempfer, H.W.; Berndt, M.; Voigtlaender, G. Estimation of Residual Service Life for Existing Sewerage Systems. 2002. Available online: http://www.irbnet.de/daten/iconda/CIB9270.pdf (accessed on 12 March 2018).
22. Zaldivar, E.C. *Settlement Agreement Final Order—Civil Action No. 01-191-RSWL and Civil Action No. 98-9039-RSWL Consolidated—2011 Sewer Odor Master Plan*; Wastewater Engineering Services Division, Bureau of Sanition: Los Angeles, CA, USA, 2011.
23. Bioteg.com. Biofilter and Odor Control Systems Products and Solutions. Available online: http://www.bioteg.com/biofilter/ (accessed on 10 March 2018).
24. Talaiekhozani, A.; Bagheri, M.; Goli, A. An overview of principles of odor production, emission, and control methods in wastewater collection and treatment systems. *J. Environ. Manag.* **2016**, *170*, 186–206. [CrossRef] [PubMed]
25. Jacobi Carbons. A Story of Success. Available online: https://www.jacobi.net/ (accessed on 14 March 2018).
26. Bionic Fuel Technologies. Available online: http://bionic-enterprises.com/bionic-fuel-technologies/ (accessed on 14 March 2018).
27. Rehau, Unlimited Polymer Solutions. Available online: https://www.rehau.com/group-en/ (accessed on 14 March 2018).
28. Biothys, Olfactive Silence. Available online: http://www.biothys.co.kr/ (accessed on 14 March 2018).
29. Subio Eko. Available online: http://www.subio.cz/sekce-5/ (accessed on 14 March 2018).
30. Grena. Available online: http://www.grena.cz/cz/ (accessed on 14 March 2018).
31. Industrial Strength Odor Control. Earth-friendly Odor Solutions. Available online: http://odormanagement.com/ (accessed on 14 March 2018).
32. Neutralizes Odors, Naturally. Available online: http://onaonline.com/ (accessed on 14 March 2018).
33. Mateson Chemical Corporation. Available online: http://badairsponge.com/ (accessed on 14 March 2018).
34. Biothys GmBH. Available online: http://www.biothys.com/home/ (accessed on 14 March 2018).
35. ČSN EN 752. *Drain and Sewer Systems Outside Buildings—Sewerage Pipelines*; Czech Office for Standards, Metrology and Testing: Praha, Czech Republic, 2017.