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Estimation of the Influence of the Sorption Properties of Selected Natural Fibres on the Efficiency of Deodorisation Processes of Industrial Waste-Gases

Abstract
This article presents the results of research into removing volatile organic compounds from waste gases while using bio-filters filled with mixtures of natural materials, such as peat, bark, jute, hemp and cotton. Experimental filtration beds were installed in a fatty-products manufacturing company above a fatty-waste catcher (a container into which waste water from all the production departments of the company were linked). The waste-gases were guided through the filtration beds. The estimation of the process efficiency was based on a chromatographic analysis of the waste-gases at the input and output of the bio-filters. The article also presents the results of investigation concerning the desorption of water solutions of cotton, jute, and hemp fibres, consisting the active part of the filters. After some months of exploiting the filtration beds, the biological material was taken from the beds and conditioned at a constant temperature up to a? constant mass. The results confirmed the differentiation of the sorption properties of the fibres used, and at the same time the differences between the efficiency of the various filters indicated by us.

Key words: *odours, deodorisation, bio-filtration, natural fibres, volatile organic compounds, gaseous fatty acids, cotton, jute, hemp.*

Introduction

Substances exist independently of gaseous substances, which are a threat for humans due to their toxic effect, which only worsens the comfort of life; however, they do not directly intoxicate human beings. Such substances, called odours, are uncomfortable for humans, even when they exist in air in very small concentrations [1].

The uncomfortable conditions related to the formation of odours in environmental air influence not only staff connected with technological processes, but also the whole environment surrounding industrial installations. Leaky industrial buildings and technological pipes, ventilation openings, lagoons and open containers, as well as chimneys are often the sources of every-day lack of comfort [2].

The first purification systems for air and industrial waste-gases in industry were based on simple filter sets which removed odorous substances and dust. Such systems are still used, but their small efficiency and fast usage have caused further development in this field. [3].

The biological degradation of odour creating air-contaminations has formed an alternative for a range of physical and physicochemical methods of air purification. The techniques of biological purification have confirmed their usability, not only for removing odours, but also other undesired compounds emitted by industry [4].

Taking into consideration their chemical character, odours are divided into non-organic and organic compounds. The first includes such gases as hydrogen sulphide, ammonia and nitrogen & sulphur oxides, whereas the second includes mercaptanes, organic bi-sulphur oxides, amines, organic acids, aldehydes, and ketones, which means compounds including hetero-atoms of sulphur, nitrogen and oxygen. Odours most often occur as mixtures of many different chemical substances,

The processing of animal wastes is among various industries that emitting odours which are especially uncomfortable and oppressive for humans. It is a source of technological and accidental emissions of ammonia, amines, hydrogen sulphide, sulphur oxides, sketoles, mercaptanes, aldehydes, organic acids, and cadaverines. Two other very oppressive industrial branches are the processing of fish products and manufacturing fish flour with the characteristic odour of tri-methylamine. The range of environmentally oppressive enterprises also includes petroleum refineries, asphalt oxidation installations, iron foundries, enterprises of the rubber and cellulose industries, with compounds such as methilmercaptan, bi-methyl sulphur oxides and hydrogen sulphide occurring, as well as animal farms, waste-water purification installations, waste deposits, and plants of the fatty industry. In some cases odorous substances occur occasionally or in particular situations, and they are even sometimes not identified as odours. The same substances existing in air in great amounts are identified as oppressive odours [5].

A layer of filtration material with micro-organisms included, which are able to biologically degrade air contaminations, is the main element which eliminates the odours in bio-filters. When gases are slowly blown through the filtration material layer, contaminations are sorbed, and next decomposed by micro-organisms. The action of micro-organisms causes the self-regeneration of the sorbent filling. [6].

The selection of filtration material is very important considering the working efficiency of a bio-filter. The filtration material should be implanted with micro-organisms, as well as characterised by a large relative surface, and loose structure, assuring small resistance to gas flow. The activity of the filtration material used for constructing a bio-filter is decisive regarding its surface and thickness of the filtration layer. Determination of the filtration material activity in relation to contamination absorption is necessary.

The literature about bio-filters, which is available, does not include detailed information concerning these questions [8].

While selecting filtration material, it is necessary to consider the grain characteristic of the filling, the porosity, the relative surface of the carrier, the air (gas) flow resistance, the ability of water retention, its durability, the odour itself, the cost, necessary maintenance activities while working and the incubation density of the micro-organisms. Among the filtration materials used in the bio-filtration of contaminated gases, the following are preferred: earth, leaves of trees, peat, compost, bark, heather, perlit, and small plastic forms [5, 8, 9].

It was found that cotton fibre can also be an alternative filtration material [10], which may be used as an additive for other components with the aim of intensifying the processes of the desideration of odorous contaminations.

In our investigation we used a mixture of peat and bark, with inter-layers of cotton, jute and hemp fibres to fill the bio-filters [11 – 14].

Methodology of investigation

As additives for the filling of peat - bark bio-filters, we used natural fibres in our investigations with the aim of improving the sorption properties of the bio-mass used.

The subject of our research was a set of natural fibres, as mentionedabove, and their sorption properties, which have a decisive influence on the efficiency of the bio-filtration processes of industrial waste-gases, including fatty acids as the basic odorous compounds. As it is known that fatty acids easily undergo biological decomposition , we assumed that a set of micro-organisms would be formed as a result of natural selection (eventually supported in the preliminary phase of the experiment).

We assumed also that the basic analytical tool, which would be used to estimate the efficiency of the process of elimination of the odours from the gases, was the chromatographic analysis of the gases. To undertake this task, a GC System HP 6890 Series Hewlett Packard gas chromatograph was used.

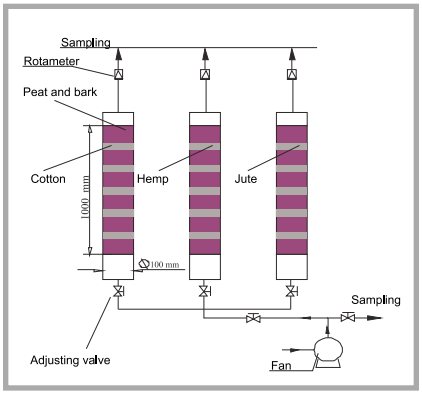

Figure 1. *Scheme of the experimental installation, including biological beds with fillings of a mixture of peat and bark, jute, hemp and cotton.*

Samples were taken in the following way:
50 l of outlet gases were guided through washers with 0.05 M KOH and a column for polar compounds: FF AP 10 m × 0.53 mm, covered by afilm of 1 μm thickness (polyglycol modified with terephtalate acid), and analysed by a flame ionisation detector (FID).

The analysis of the deodorisation effects was based on comparing the chromatograms obtained by the analysis before and behind the filtration bed.

The investigations were carried out directly in the fatty-products plant on a semi-industrial scale. Quantitative changes in the substances contaminating waste-gases from the fatty catcher were measured after guiding the gases through a bio-filter with an addition of natural fibres.

A scheme of the installation is presented in Figure 1.

The beds were formed in colourless pipes made from polymethylmetacrylate (PMMA) with a diameter of 100 mm and length of 1000 mm. Each of the bio-filters was closed from the top by a cover equipped with a half-inch pipe with a ball valve at its end; in this way, all the gases went through the bed and were directed to pipes which led them to the atmosphere.

The bio-filters were filled with biomaterial composed of a mixture of peat and bark; six sub-layers of this material, each of 300 g were separated by five spacers with natural fibres, each of them of 5 g. Three kinds of beds were prepared: with separators of cotton, hemp, and jute. The volume of each of the bio-filters was 0.007 m^3, whereas the surface cross-section of the bed was 0.008 m^2.

The layers of the biological beds were suspended at a height of 10 cm from the bottom of the pipe on a mesh made from stainless steel. Gas was fed from the bottom of the pipe (Figure 1).

The biological load of the beds was 125 $m^3/m^2/h$. The time of stopping the gas flow in the bed was about 25 seconds.

Gases from the fatty catcher were transported by a van and then through half-inch pipes to their respective biological beds. Adjusting valves were installed before the beds with the function of enabling the equalisation of the flow rates through all three beds. A rotameter of the RDS 15 type was installed after each filter, and used to measure the flow rate as well as to sample the gases after deodorisation.

In order to determine the absorbtivity of the fibre layers used as separators in the biological beds, each of the 5 fibre samples designated for testing were weighted and next conditioned in a drier at a temperature of 105^0C for 30 minutes. These actions were repeated until a dry mass of the samples was attained. The absorbtivity C was calculated by equation (1):

$$C = \frac{m_w - m_s}{m_s} \cdot 100 = \frac{m_{nw} - m_n}{m_{ns} - m_n} \cdot 100 \quad (1)$$

where:
C - absorbtivity, in %,
m_w – sample mass after conditioning, in g,
m_S – sample mass after conditioning, in g,
m_n – mass of the empty cell, in g, and
m_{nw} – mass of the cell with sample after conditioning (after drying to constant mass, in g.

Additionally, the conditioning the process was carried out with the use of a WPS 210S weighting drier from the company RADWAG. The measurements were conducted in the MOD 3 mode, at a temperature of 75 °C. The conditioning was based on the absorption of infra-red radiation by the fibre sample, achieved with the use of appropriate IR-radiators. The absorption of IR-radiation caused an increase in the internal energy of the fibres and evaporation of moisture.

In order to check in what way the absobtivity of the cotton, jute and hemp fibre layers, comprising the biological beds, the changes with timeand approximations of the dependencies investigated were evaluated by the regression function in logarithmic form (2):

$$\hat{C} = A_1 \cdot \ln t + A_2 \qquad (2)$$

Values of the regression function factors were estimated by minimalisation of the sum of the deviation squares.

In order to check if the regression functions determined are statistically significant the following quantities were calculated:

1. The multidimensional correlation factor R expressed by equation (3) [16]

$$R = \sqrt{\frac{\sum_{i=1}^{n}(\hat{C}_i - \overline{C})^2}{\sum_{i=1}^{n}(C_i - \overline{C})^2}} \qquad (3)$$

where:

C – value of the regression function determined at the i-minute of the sample conditioning,

C_i – absorbtivity of the sample at the tenth minute of its conditioning, and

C – average absorbtivity of the sample.

2. Value of the Fisher – Snedocor statistic calculated according to equation (4) [16]:

$$F_{obl} = F(K; N-K-1) = \frac{N-K-1}{K} \cdot \frac{R^2}{1-R^2} \qquad (4)$$

where:

K – number of regression function coefficients without the coefficient of the absolute term which equals K = 1,

S – number of readings of the fibre sample mass in subsequent determinations of its drying, recorded every 0.5 hours.

With the aim of obtaining a regression equation ,which would be usable for the description of the absorbtivity of the fibre layers used in the bio-filters, and at the same time fulfilling the significance requirements at a determined probability level (p = 0.95; α = 0.05), the following output condition should be fulfilled [16 –17]:

$$F_{obl} = F(K; N-K-1) \geq F_{kr}, \qquad (5)$$

where:

F_{kr} – critical value of the F-Snedocor statistic taken from the Fisher-Snedocor distribution table at a significance level of α = 0.05, and at a degree of freedom K and N – k – 1.

Research results

The samples of waste-gas taken before and after the peat – bark beds which included separating layers of fibrous materials, such as jute, cotton and hemp, were transported through washers containing 5 ml of 0.05 M KOH. The gas flow rate was 100 l/h, and the time of sampling was 30 minutes. After acidification with 1M HCl and injection of 2 µl of the sample into the sample injector of the chromatograph, we obtained the diagrams presented in Figures 2 – 4, As a result of the measurements carried out, we obtained chromatograms and concentration values of the contaminations which caused the odorous character of the waste-gases, Only three of the most odorous fatty acids were analysed, which were acetic acid (C2:0), propin acid (C3:0) and butyric acid (C4:0).

Figures 2, 3, and 4 present the results of chromatographic investigation of the gaseous samples after 11 weeks of experimental exploitation of the bio-filters, which was during stable working of the beds.

After three months of exploitation and investigation of the bio-filters with separators filled with cotton, jute and hemp fibres, representative samples were taken and next conditioned in a drier at a temperature of 100^0C. The average of the values obtained for the fibre masses of the conditioner , together with the cells which contained the samples, are presented in Table 1.

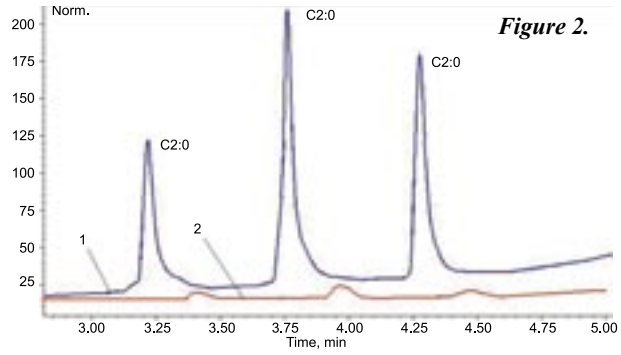

Figure 2.

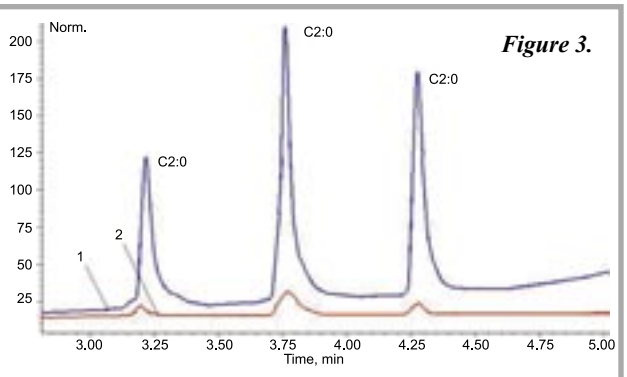

Figure 3.

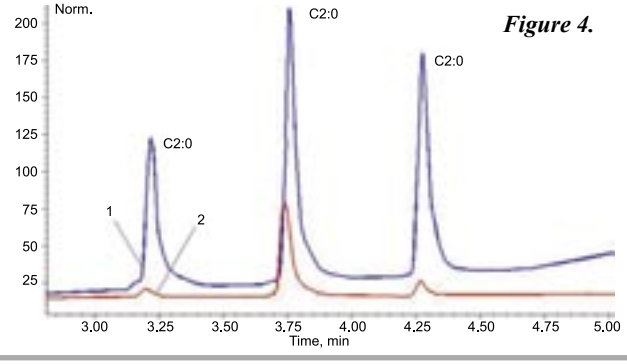

Figure 4.

Figure 2. *Chromatograms of gases analysed before (1) and after (2) deodorisation (after being transmitted through the peat - bark bed with cotton) after 11 weeks of filter exploitation.*

Figure 3. *Chromatograms of gases analysed before (1) and after (2) desodorisation (after being transmitted through the peat-bark bed with hemp) after 11 weeks of filter exploitation.*

Figure 4. *Chromatograms of gases analysed before (1) and after (2) desodorisation (after being transmitted through the peat-bark bed with jute) after 11 weeks of filter exploitation.*

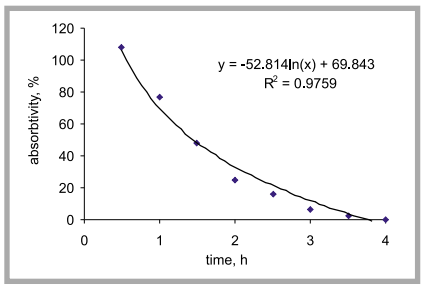

Figure 5. *Regression function of the cotton fibre absorbtivity.*

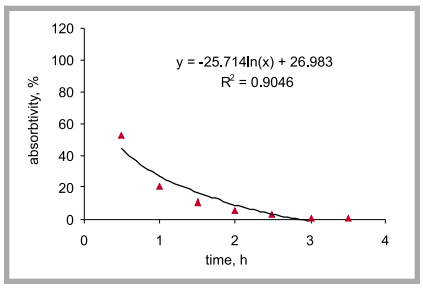

Figure 6. *Regression function of the jute fibre absorbtivity.*

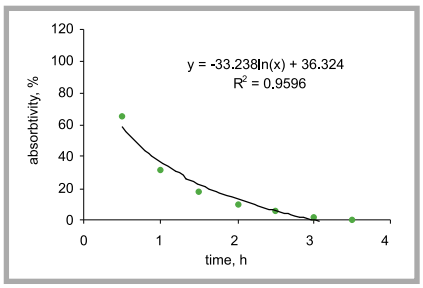

Figure 7. *Regression function of the hemp fibre absorbtivity.*

On the basis of these results, the absorbtivity of the samples was calculated. The values obtained are shown in Figures 5 – 7 in the form of dependencies of absorbtivity for the sample conditioning time.

Analysis of the results

The concentration changes in the most odorous volatile fatty acids (acetic acid, propin acid and butyric acid), which the waste-gases contained and were deodorised in the bio-filters, were estimated. The concentration changes in these acids, which occurred in the deodorisation process of the gases, are listed in Table 2.

Table 1. *Fibre mass during conditioning.*

conditioning time, h	Sample mass with cell, g		
	cotton	jute	hemp
0	67,7293	92,2836	72,7823
0.5	66,8398	91,8971	72,3212
1.0	66,5182	91,5823	72,0189
1.5	66,2254	91,4863	71,8989
2.0	65,9856	91,4356	71,8238
2,5	65,8917	91,4165	71,7912
3,0	65,7988	91,3923	71,7527
3,5	65,7527	91,3921	71,7398
4,0	65,7317	91,3824	71,7387
4,5	65,7311	91,3824	71,7387
5,0	65,7298	-	-
5,5	65,7298	-	-

After 11 weeks of bio-filter working time, the changes which occurred during their exploitation and in the biological conditions began to stabilise. Equilibrium could be identified between the loading of the bed and the possibilities of the micro-organisms already specialised/involved in the changing of fatty acids into water and bi-carbon oxide. The beds achieved a relatively high percentage of odours removed. In the case of the beds with hemp and jute, the waste-gases were deodorised by 90% and 80% , respectively.

The bio-filter with the bed containing peat, bark and cotton was identified as the best, with an efficiency of 95%, which for small concentrations of odorous substances is a very optimistic result. The concentration of acetic acid in the waste-gases decreased from 2440 μg/m^3 to 212 μg/m^3 after guiding it through the bed containing cotton fibres, and it went down to 227 μg/m^3 after deodorisation by the bed containing hemp fibres. However, after deodorisation by the bed with jute fibres the concentration went down to 203 μg/m^3.The concentration of propin acid, which in unpurified gas was 5311 μg/m^3, after the process of deodorisation decreased to 539 μg/m^3, 1219 μg/m^3, and 468 μg/m^3 while being guided through the bed containing hemp, jute and cotton, respectively. The butyric acid was decreased after deodorisation from 4708 μg/m^3 down to 388 μg/m^3 by the beds with hemp and 298 μg/m^3 by the beds with jute, respectively. The concentration of butyric acid in the gas tested, after deodorisation by the bed containing cotton, was below the limit of determination of the estimating method used.

The total concentration of volatile fatty acids was 12,460 μg/m^3 before the deodorisation process, whereas after deodorisation it was 1,154 μg/m^3, 1,720 μg/m^3, and 680 μg/m^3 for the peat - bark bed with hemp, jute, and cotton, respectively.

Analysing the conditioning results obtained and presented in Figures 5 – 7 we can state that the greatest absorbtivity, at the moment of being taken from the biological bed, was characterised by the cotton fibre samples, whereas jute by the smallest. The absobtivity of the cotton sample before conditioning was about 193%, jute fibres 91% and hemp fibres 117%. The cotton fibres were conditioned the longest, which means about 5.5 h. The hemp and jute fibres were conditioned to constant mass for about 4.5 h. The decrease in the absorbtivity over the first 30 minutes of conditioning the cotton was over 180%, whereas in the case of jute and hemp it was about 40%. During subsequent minutes, the absorbtivity of the samples decreased by a value equal to half of the latter's absorbtivity.

Additional conditioning carried out with the use of the WPS 210S weighting-drier from the company RADWAG, confirmed that the absobtivity of the respective samples determined by this method was comparable with the values obtained by conditioning in the drier at a temperature of 105 °C. For the cotton fibres it was on average 214%, for jute 88% and for hemp 140%. The process of conditioning

Table 2. *Concentration of the acetic acid, propin acid and butyric acid before and after the process of deodorisation, after 11 weeks of exploitation of the beds. *The determination limit of the methods was 206 μg/m^3.*

Efficiency and concentration of:	Concentration			
	before deodorisation, before the beds	after deodorisation		
		peat – bark bed with hemp	peat – bark bed with jute	peat – bark bed with cotton
acetic acid C2:0, μg/m^3	2,440	227	203	2125
propin acids C3:0, μg/m^3	5,311	539	1219	468
butyric acid C4:0, μg/m^3	4,709	388	298	below determination limit *
total, μg/m^3	12,460	1,154	1720	680
efficiency of the bed, %		90	86	95

Table 3. *Parameters of the regression function.*

Humidity of the sample	analysed function	regression coefficient		statistic value			
		A_1	A_2	R^2	R	F_{obl}	F_{kr}
cotton	$W_b = f(t)$	-52.814	69.843	0.9759	0.9879	242.96	5.99
hemp	$W_k = f(t)$	-33.238	36.324	0.9596	0.9796	118.76	6.61
jute	$W_j = f(t)$	-25.714	26.983	0.9046	0.9511	237.05	6.61

by this method lasted on average 30 minutes in the case of cotton, 25 minutes for jute, and 23 minutes for hemp.

From the above-mentioned test data, we can conclude that cotton absorbed a greater amount of water together with substances dissolved in it (fatty acids, among others) than the remaining fibres. This indicates the better sorption properties of these fibres, and confirms literature data.

In order to check in what way the absorbtivity of cotton, jute, and hemp fibres, which are part of the biological beds, the changes with conditioning time and approximation of the dependencies investigated were evaluated by the regression function presented in Figures 5-7.

In Table 3 the parameters of the regression function approximated with the use of a logarithmic function are listed.

Analysing the data listed in Table 3, we can state that all the functions of sample absobtivity changes determined during their conditioning are statistically significant. The coefficients of the multi-dimensional correlation R are characterised by high values (0.95 – 099), and the values of the F-Snedecor statistics calculated are many times greater than the critical values taken from the F-Snedocor distribution tables at a significance level of $\alpha = 0.05$, and at a degree of freedom of K and N – K = 1 = F_6^1 – 5.99 and $F_5^1 = 6.61$.

The statistical analysis indicated that the absobtivity of the fibre layers by which the biological beds are characterised, irrespective of the kind of the fibres applied, decreases logarithmically with the time of their conditioning.

Analysing the results obtained, we can conclude that the layer consisting of cotton fibres absorbed water to a greater degree than the layers of jute and hemp. Furthermore, it should be emphasised that during conditioning, the layer of cotton fibres, at a temperature of 105 °C, gave up humidity significantly more slowly than the other fibres investigated. This proves that in this case water is more stably bound with the fibre matter. This fact may confirm the presence of micro-cracks and micro–pores on the surface of the fibre, from which it is relatively more difficult to remove the water absorbed. From these facts a conclusion can be drawn that a cotton fibre layer has better sorption properties than jute and hemp fibre layers. This means that the application of separators with cotton fibres influences in a greater amount the efficiency of peat – bark bio-filters more than the application of separators of other fibres.

Conclusions

1. The effects of bio-filtration depend on the kind of filtration material applied.
2. Natural fibres, such as cotton, hemp and jute may be successfully used as an additive to beds applied as fillings for bio-filters. The results of the investigations carried out by us into removing odour-creating substances from waste-gases occurring in the fatty product industry confirmed the great effectiveness of the bio-filtration process with the use of the above-mentioned- fillings..
3. Cotton fibres are characterised by the best sorption properties among all the natural fibres tested by us. Considering the nature of the bio-filtration process, we can conclude that the more water sorbed by fibres, the more fatty acids can be dissolved in them, and better conditions will exist for the development of micro-organisms, which increase the gas deodorisation. The resects/results of the desorption carried out also show differences during the drying of certain fibres, and in their percentage loss of mass. This is caused, among others, by the smaller content of lignins and pectins in cotton fibres as compared to hemp and jute fibres.

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