Vaidotas VAIŠIS

INVESTIGATION AND EVALUATION OF BIOSORBENTS FOR OIL PRODUCTS

Summary of Doctoral Dissertation

Technological Sciences,
Environmental Engineering and Landscape Management (04T)

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Vilnius 2005

VILNIUS GEDIMINAS TECHNICAL UNIVERSITY

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VILNIAUS GEDIMINO TECHNIKOS UNIVERSITETAS

Vaidotas VAIŠIS

NAFTOS PRODUKTUS SUGERIANČIŲ BIOSORBENTŲ TYRIMAS IR ĮVERTINIMAS

Daktaro disertacijos santrauka

Technologijos mokslai, aplinkos inžinerija ir kraštotvarka (04T)

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General Characteristics of the Disertation

The Problem

The main pollutants that affect the soil are organic compounds (oil and its products, grease, etc), metal compounds, and household waste. Comparing with oil and its products, the extent to which household waste and grease pollute the soil is lower. Besides, at present, in Lithuania major attention is paid to oil and its products' elimination from the soil.

The soil is polluted with oil when different oil products get into it (fuel oil, mineral solutions, naphtha, petrol). Oil products can get into the natural environment because of the following human activities:

- during transportation of oil products – due to railway, tank trucks, ship, and supply route accidents, and leaky junctions;
- maintaining these resources in internal combustion engines, cars, railway locomotives, ships, and aircrafts;
- machine production, building materials, chemistry, agricultural industries;
- carrying out work related to motor-transport, railway, ship, and aircraft repairs;
- during oil product filling, re-filling at petrol stations and oil terminals;
- maintaining oil product extraction fields;maintaining military training grounds and performing military activities.

Recently, in Lithuania, the same as in other countries, oil products are among the pollutants that mostly affect earth entrails and water. Direct researches have already revealed more than 300 cases of pollution of earth entrails with oil products. Soil and groundwater is polluted almost at all oil product storage facilities or realisation sites (oil base, petrol stations, boiler-rooms, etc.), the number of which is several thousands in Lithunia. Oil and its products pollute seas and oceans. This pollution is mainly caused by oilfield maintenance, intensive navigation, transportation of crude oil ands its products.

Taking into account the extent, harmfulness, and pollution elimination measures and costs, it could be stated that pollution with oil products is a topical ecological problem.

Topicality of the Work

Due to anthropogenic economic activities, the oil that is spilled into the natural environment makes a great damage. Oil and its products, when in the water and soil, may localise and form films or may disperse forming oil and water emulsions and get partially dissolved.

Most of the areas that are polluted with oil products are usually located within the sanitary protection zones of water-places, in which pollution of earth entrails inevitably reduces resources of such water-places and worsens their quality. When oil gets into the water, a ton of oil products disperses in the area of 12 km^2. The formed film prevents oxygen from getting into the water. When concentration of oil products is 0.1 mg/l, fish meat gains an unpleasant smell elimination of which is impossible even with the help of technological processes. When concentration of oil products in the soil is 2 g/kg, the plant vegetation gets disturbed and morphological alterations occur.

When oil products get into the environment, pollutant localisation first of all is performed. Sorbents are employed for that. Thus the stores of sorbents are necessary in the places of potential pollution with oil products. In order to assess the sufficiency of the amount of these materials, detailed tests of oil product sorption are necessary. Besides, sorbents should comply with the environmental requirements: they should be easily collected, cause no damage even when they remain in nature, they should be biodegradable, and have potential for utilisation. Biosorbents produced of natural resources comply with all of these requirements.

Oil that is spilled during an accident causes the greatest damage to the nature, thus it is necessary to carry out complex tests of measures intended for pollution elimination.

Goal and Objectives of the Work

The goal of the paper is to carry out complex tests of biosorbents that absorb oil products and to analyse the sorbtion process using local raw materials for the elimination of the spilled oil products.

Objectives of the paper:

- to assess the sorption properties of materials used for the elimination of oil products;
- to identify the optimal material for the production of a sorbent of local raw materials;
- to carry out complex experimental tests of a sorption process;
- to find out the physical parameters of sorbents of oil products;
- to carry out experimental tests of water absorption;
- to carry out tests of the efficiency of sorption off the water surface;
- to find out the residual part of the material being sorbed;
- to carry out experimental tests of the full capacity of sorption;
- to carry out tests of thermal modification of biosorbents;
- to find out the impact of sorbent fraction on the sorption properties;
- to carry out experimental tests of cleaning of the polluted water with the help of biosorbents;
- to perform a mathematical modelling of the sorption process.

Novelty of the Work

The novelty of the paper lays in the complex test of oil product biosorbent covering a theoretical analysis of the sorption process, and experimental and computer modelling. The dissertation analysis the possibilities of employing Lithuanian materials in the production of biosorbents. For that:

- a review of materials used for oil product pollution elimination has been performed;
- the optimal material for the production of a sorbent of local raw materials has been identified;
- methodology for experimental tests have been developed and applied;
- oil product biosorbents have been defined and examined in a complex way;
- during researches, experimental tests were performed on the absorption of water by a different fraction biosorbent, efficiency of sorption off the water surface, finding out of the residual part of the material being absorbed, and on the full capacity of sorption;
- experimental tests of thermal modification of a sorbent that established the optimal regime of heating have been performed.
- experimental tests of a biosorbent as a filter charge for cleaning polluted water have been performed; the efficiency of filtration under different charge heights and filtration speed have been found out.

Practical Value of the Work

The carried out experimental tests and the results obtained in the course of them have revealed that a sorbent produced of local raw materials could be successfully used in the elimination of oil product spillage. By its sorption properties, a biosorbent outfaces industrial sorbents; besides, it may be used in a complex way, i.e. it may be used for collection of oil products off the soil and water surfaces and it may be used as a filter charge of polluted water.

Based on the tests, a patent application "Biosorbent" has been submitted for a patent of the Republic of Lithuania. A decision has been approving and a patent application has been announced in the Newsletter No. 1 (2005) of the State Patent Bureau.

Approbation of Results

A graduate student has published 11 scientific publications: 1 scientific article in a foreign magazine with ISI Citation Index; 2 scientific articles in foreign magazines; 3 scientific articles in magazines included into the LL list; 5 scientific articles in other press of Lithuania.

The results of the thesis have been discussed at 3 international conferences and 4 republican scientific conferences; besides 4 scientific publications have been included into conference report materials.

Extent and Structure of the Work

The thesis consists of an introduction, 7 chapters, general conclusions, list of references to literature, author's publications and reports on the subject of the paper. The paper consists of 141 pages of the text, 73 figures, and 4 tables.

1. Materials that Absorb Oil Products and Technologies of Their Application

The list of references to the literature dealing with the materials that absorb oil products shows that the optimal sorbents must comply with the environmental requirements: they should be easily collected, cause no damage even when they remain in nature, they should be biodegradable, and have potential for utilisation.

2. Examination of Physical and Sorption Properties of Sorbents

Summarizing experimental investigation of sorbents – Qualisorb gold 628, Sphag-sorb, USVR-VIP, Belneftesorb-extra and biosorbent from Lithuanian *sphagnum recurvum*, the summary Table 1 describing sorbent characteristics has been conluded.

Table 1. Summary of comparative characteristics of sorbents

Sorbent / Characteristics	Sphag-sorb	Qualisorb gold 628	Belnefte-sorb extra	Biosorbent from Lithuanian sphagnum recurvum	USVR-VIP
Density [g/cm^3]	0.199	0.400	0.254	0.175	0.0066
Water sorption after 24 h [g of water / g of sorbent]	**3.92 (2)**	**-**	**1.05 (3)**	**14.1 (1)**	**1.01 (5)**
Diesel-fuel sorption from water surface [g of diesel fuel / g of sorbent]	**3.74 (3)**	**-**	**3.54 (1)**	**8.4 (4)**	**51.4 (5)**
Petrol sorption from water surface [g of petrol / g of sorbent]	**4.00 (3)**	**-**	**2.84 (1)**	**7.2 (4)**	**51.6 (5)**
Maximal total sorption of diesel fuel [g of diesel fuel / g of sorbent]	**5.50 (3)**	**1.44 (1)**	**4.90 (2)**	**9.9 (4)**	**55.0 (5)**
Maximal total sorption of petrol [g of petrol / g of sorbent]	**5.60 (3)**	**1.50 (1)**	**4.40 (2)**	**7.9 (4)**	**60.0 (5)**

Explanation: (1) – the lowest indicator; (5)- the highest indicator.

The data presented in Table 1 show that the sorbent Qualisorb gold 628 has the greatest density. This is determined by its origin – it is produced from natural mineral diatomite and crystal quartz. Mineral origin of this sorbent is shown also by the greatest density of sorbent particles – 1.074 g/cm^3. The sorbent USVR-VIP has the lowest density – 0.0066 g/cm^3. This is a very fine, light and loose sorbent produced from activated carbon. Sorbents Sphag-sorb and Belneftesorb-extra and biosorbent from Lithuanian *sphagnum recurvum*, have similar density – 0.199 g/cm^3, 0.254 g/cm^3 and 0.175 g/cm^3 correspondingly. The sorbent Sphag-sorb is produced from peat-moss (sphagnum). Belneftesorb-extra – from peat and biosorbent from Lithuanian *sphagnum recurvum*. Therefore, they are close by their origin.

The lowest water sorption is that of the sorbent USVR-VIP – 1.01 g/g, the highest one is of a biosorbent – 14.1 g/g.

When investigating sorption of diesel fuel from water surface, the inverse sorption trend comparing to that of water is observed: at the beginning of the experiment, sorption is very intensive.

The highest sorption of diesel fuel (g of oil products / g of sorbent) is shown by USVR-VIP – 51.4 g/g. The sorbents Sphag-sorb and Belneftesorb-extra have similar sorption values – 3.74 g/g and 3.54 g/g correspondingly. Biosorbent from Lithuanian *sphagnum recurvum* shoved very hight sorption value – 8.4 g/g.

When analyzing petrol sorption from water surface, similar trends are observed as that in diesel fuel case.

The highest sorption of petrol (g of oil products / g of sorbent) is shown by USVR-VIP – 51.6 g/g. The Sphag-sorb shows 4.00 g/g and this value is higher than that of Belneftesorb-extra – 2.84 g/g. Biosorbent from Lithuanian *sphagnum recurvum* again shoved very hight sorption value – 7.2 g/g.

The highest maximal diesel-fuel sorption coefficient is shown by USVR-VIP – 55 g/g, and that for petrol – 60 g/g.

The sorbent Sphag sorb has the maximal sorption coefficient for diesel fuel - 5.5 g/g, and that for petrol – 5.6 g/g, and these coefficients are higher than that for the sorbent Belneftesorb-extra: sorption coefficient for diesel fuel – 4.9 g/g, that for petrol – 4.4 g/g.

Biosorbent from Lithuanian *sphagnum recurvum* has the maximal sorption coefficient for diesel fuel – 9.9 g/g, and that for petrol – 7.9 g/g, and these coefficients are higher than Sphag-sorb and Belneftesorb-extra.

The lowest maximal sorption coefficient is shown by Qualisorb gold 625: for diesel fuel – 1.44 g/g, for petrol – 1.50 g/g.

High maximal sorption of the sorbent USVR-VIP is determined by its very low density – 0.006 g/cm^3. And this means 1 g of the sorbent takes 166.7 cm^3 of volume, when 1 g of the sorbent Sphag-sorb – only 5.0 cm^3.

The highest efficiency of oil-product collection from smooth surface is shown by the sorbent USVR-VIP – sorption efficiency reaches 95 % at sorption coefficient equal to 38.0 g/g. Rather high sorption efficiency is shown by the biosorbent from Lithuanian *sphagnum recurvum* - sorption efficiency reaches 95 % at sorption coefficient equal to 7.3 g/g.

The experimental tests have revealed that by its sorption properties a sorbent produced of local materials overtakes its foreign analogues. The presented sorbents are closely related by the origin of material.

An ecologically clean biosorbent, intended for the collection of oil products both off the water surface and off the soil surface. Collecting oil products with the help of sorbents, it is inevitable that part of a sorbent remains in the environment. A biosorbent, even when left in nature, is known for its biodegradable properties.

3. An Impact of a Biosorbent Fraction on Sorption Properties

Examining absorbing materials (sorbents), it has been noticed that the size of sorbent particles has great impact on the efficiency of sorption. In order to analyse the impact of the size of peat-moss fraction on the capacity of a biosorbent to absorb oil products, experimental tests have been performed with different fraction moss:

1) the average size of biosorbent particles up to (3–5) mm;
2) the size of biosorbent particles up to 1 mm.

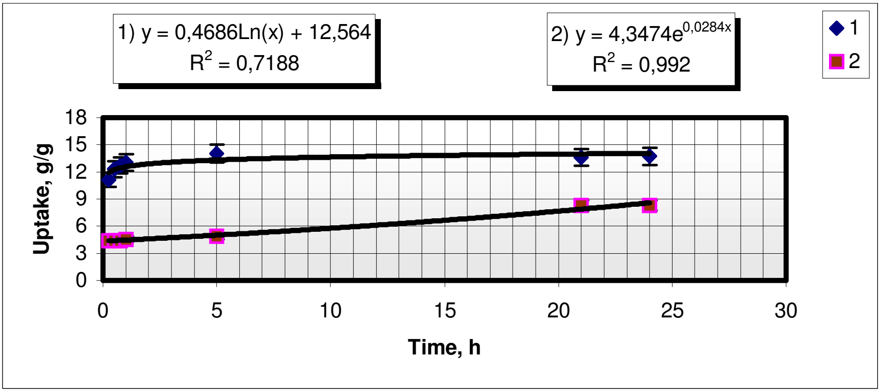

Fig 3.1. Dependence of water absorption on the time: 1 – peat-moss with the average fraction size of (3–5) mm; 2 – peat-moss with the average fraction size up to 1 mm

The obtained experiment results reveal that the fraction size of sorbents has a considerable impact on the water sorption by sorbents. Experiments with a finer fraction biosorbent show a more intensive increase in the absorption in the course of time when compared with coarser fraction sorbent. However, at the beginning of water absorption experiment, a more intensive water absorption change is seen in the first-type sorbent (from 11 g/g at the beginning of the process to 14 g/g 5 hours after overspread of the sorbent). At the beginning of the experiment, water absorption of the second-type sorbent is 4.4 g/g and during 5 hours it increases to 4.8 g/g. But within the time span from 5 to 24 hours the water absorption of the above-mentioned sorbent increases to even 75 % and reaches 8.4 g/g.

As it is seen in the given graphs, moss of a finer fraction absorbs less water than that of a courser fraction. This to a large extent is determined by porosity of this sorbent and higher density. Besides, lower absorption may be conditioned by sinking of a smaller sorbent during the experiment and its rather complicated collection (part of the sorbent that absorbs water has remained unassessed).

Figure 3.2 gives the results of diesel fuel absorption off the water surface during the experiment. As it is seen in the obtained curves, the regularity of diesel fuel absorption by sorbents of both fractions is equal. An insignificant change in the absorption in the course of time is observed. The same as in the case of water absorption, the first-type sorbent has a more efficient sorption potential. The absorption of diesel fuel by this sorbent is 25 % higher than that by a finer fraction sorbent.

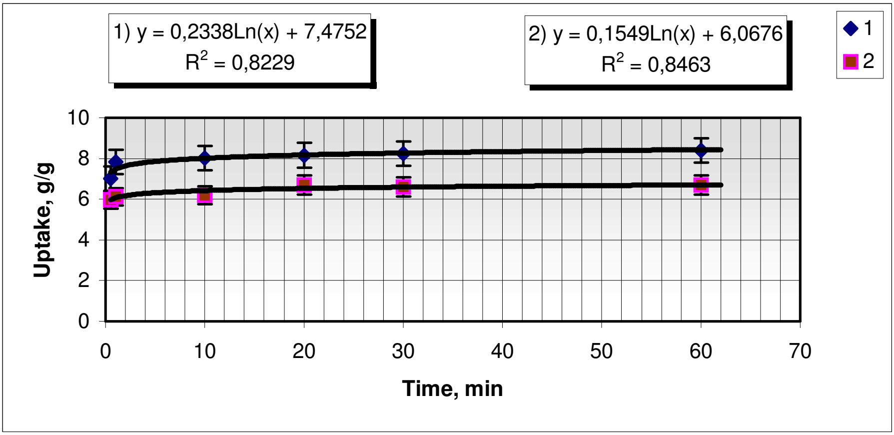

Fig 3.2. Dependence of diesel fuel absorption on time: 1 – peat-moss with the average fraction size of (3–5) mm; 2 – peat-moss with the average fraction size up to 1 mm

Absorption of petrol off the water surface by both sorbents (Figure 3.3) shows a general tendency, i.e. the absorption rapidly increases in the course of time. Here, like during the experiment of diesel fuel absorption, a sorbent of coarser fraction has better sorption properties (the absorption is on the average 22% higher that that by a finer fraction sorbent).

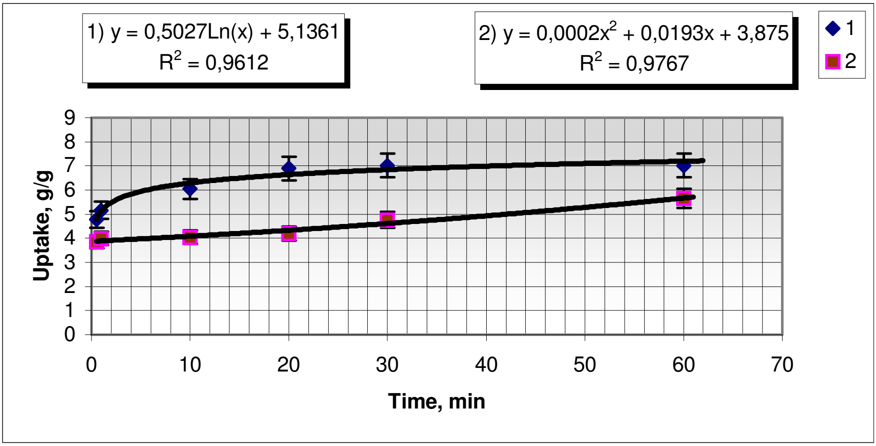

Fig 3.3. Dependence of petrol absorption on time: 1 – peat-moss with the average fraction size of (3–5) mm; 2 – peat-moss with the average fraction size up to 1 mm

The experimental data of the sorption efficiency off an even surface reveal that the sorption efficiency of oil products by both fraction sorbents is very similar. In this case, a sorbent of finer fraction is superior. This could be explained by a better contact of finer fractions with the experimental surface.

The analysis of the experimental results shows that of all the three sorption materials in question, peat-moss has the best sorption properties and their average fraction is (3–5) mm. However, this fraction sorbent has a negative feature – a rather high water absorption. This is not useful when a sorbent is used for oil product collection off the water surface. In this case, it is better to use a finer fraction moss sorbents the fraction size of which is up to 1 mm. But when choosing a material for sorbent production, it is necessary to take into consideration the fact that a sorbent should be easily overspread and gathered after oil product sorption. Gathering of a sorption material of very fine fraction is rather complicated and part of the sorbent, which has absorbed oil products, inevitably remain in nature.

4. Experiments of Thermal Modification of a Biosorbent

Collecting oil products from the water surface, water absorption is inevitable. This has impact on the sorbent's sinking in the water and worsens its capacity to accept oil products. Previous experimental tests have revealed that a biosorbent produced of peat-moss growing in Lithuania effectively absorbs oil products off the water surface, however, their water absorption is rather high (14 g of water / g of a biosorbent). In order to reduce water absorption, impregnation or other modification of a sorbent is necessary. Performing impregnation in a sorbent, chemical materials occur that, in case if a sorbent remains in nature, increase pollution. Thermal modification is one of the most promising ways of modification without including additional chemical materials. During heating, chemical alterations form in a biosorbent (disintegration of –COOH and –OH free radicals), which have impact on attachment of water molecules. Reduction in the number of these free radicals results in lower water absorption. A biosorbent produced of peat-moss is very combustible, thus it is technologically essential to set a safe heating temperature and time.

Sorbent is put on special heating saucers and placed into a thermostatic oven. The temperature is gradually raised by 3 ^{o}C per minute till it reaches 150, 200, 225, 250, 300 ^{o}C. Heating duration is 60 min.

After each heating chemical changes occurring in the biosorbent structure are estimated with the help of IR spectrometer. At the same time water and oil product (petrol and diesel) soaking capacity of the biosorbent is examined.

When an optimal heating temperature is defined, an experiment on the heating time is performed. At a certain temperature (an optimal one) the sorbent is heated for 10, 30, 60, 120, 180 min.

At 250 ^{o}C – 300 ^{o}C carbonisation of the biosorbent was noticed. Thus, heating of the sorbent at 225 ^{o}C (heating duration 120 and 180 min) and 250 ^{o}C (heating duration 10, 30 and 60 min) was given a deeper analysis.

After heating a biosorbent at different temperatures, water and oil product absorption was observed after 60 min of heating at different temperatures (Fig 4.1).

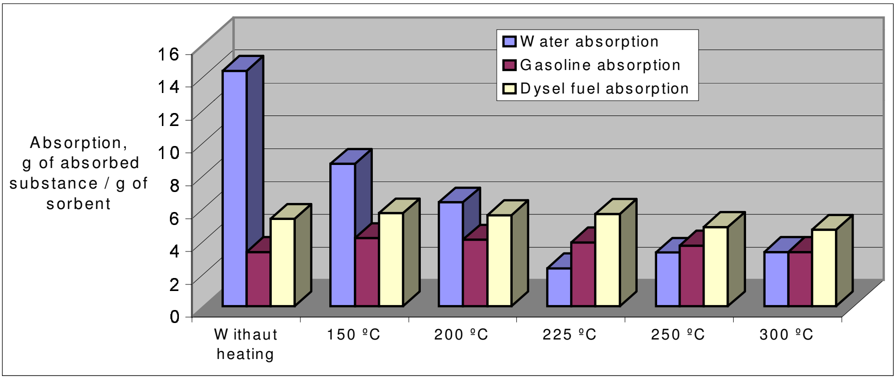

Fig 4.1. Absorption of water and oil products after 60 min of heating at different temperatures

As seen in Fig 4.1 increase of temperature results in a gradual decrease of water absorption to 2.31 l of water / g of a biosorbent (at a heating temperature of 225 ^{o}C). At a heating temperature of 250 ^{o}C and higher water absorption starts increasing – 3.26 g/g and 3.33 g/g (g of water / g of a biosorbent).

Such an increase in absorption is determined by the fact that charring of biosorbents starts at these temperatures. This results in disintegration of a porous structure of a sorbent, and it disintegrates into fine particles. Water fills the total outer surface of the sorbent, and particles, having no more pores, start sinking into water.

Analysing the data of IR spectrum analysis, chemical changes were noticed in the biosorbent structure. After systematizing the research data, graphs of IR spectrum analysis were made, where the intensity of IR rays passed through the sample expressed by the absorption coefficient is given on the ordinate axle and the number of waves (cm^{-1}) is given on the abscissa. This dimension is used due to its direct proportionality to IR ray frequency, as the main attention is focused on the sphere of hydroxide absorption waves (wave numbers 3500 – 3300 cm^{-1}) and on the sphere of absorption waves of carbon group (wave numbers 1740 – 1600 cm^{-1}).

No major structural changes were noticed in the sphere of carbon group absorption waves (wave numbers 1740 – 1600 cm^{-1}) at different biosorbent heating temperatures – the peak of absorption curves does not change. This could be explained by the absence of esters in the moss sorbent structure. Esters have the greatest influence on carbon combination breakage in the IR ray sphere. Disappearance of absorption waves at 3000 cm^{-1} wave number shows the disintegration of C–O combination. This reveals the total charring of the biosorbent. The start of charring and disintegration of hydroxide may be seen by observing disintegration of C–O–H combination at the wave numbers 1000 – 1050 cm^{-1}. Decrease in absorption waves is seen at a heating temperature of 250 ^{o}C which indicates the start of biosorbent charring. Charring of the biosorbent in thermal modification is unacceptable, as the structure of sorbent skeleton and pores disintegrate, and inflammation of the sorbent may occur. To have a more specific definition of a marginal heating temperature, extra heating of the biosorbent at 225 ^{o}C for 180 min, 225 ^{o}C for 120 min, 250 ^{o}C for 10 min and 250 ^{o}C for 30 min was performed. IR absorption wave show that when the biosorbent is heated at 225 ^{o}C, disintegration of C–O combinations is not noticed (wave numbers 1000 – 1050 cm^{-1}). After 10 min of heating the absorbent at 250 ^{o}C, a decrease in the number of absorption waves was noticed (wave number 1000 – 1050 cm^{-1}). This means the beginning of disintegration of C–O combinations. Thus, 250 ^{o}C is a critical temperature when performing thermal modification.

5. Experimental Tests of Cleaning of Polluted Water With the Help of a Biosorbent

During previous experimental tests, good oil product sorption properties of a biosorbent have been noticed. This allowed a conclusion that this material could be used as a filter charge for rain wastewater cleaning.

Experimental tests were performed in February 2005 at the laboratories of the Departments of Water Management and Environment Protection, VGTU. The principle scheme of an experimental test stand is illustrated in Figure 5.1.

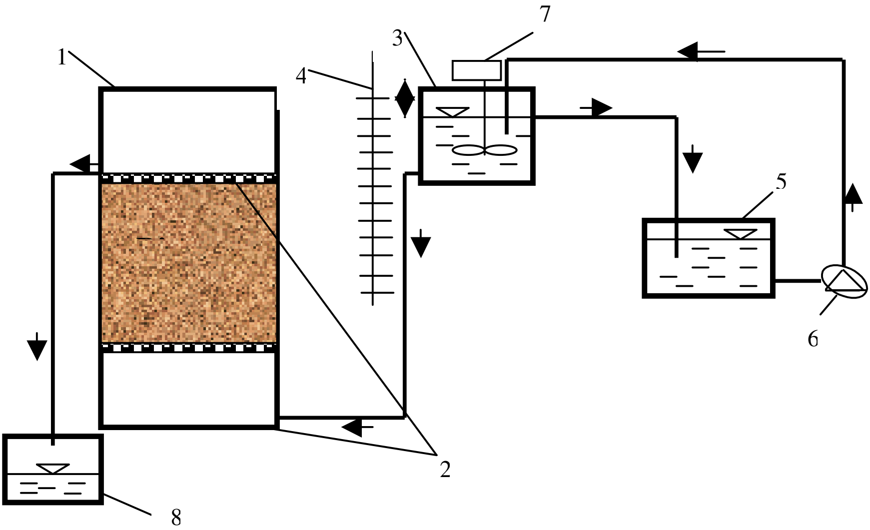

Fig 5.1. The principle scheme of an experimental test stand

The experimental test stand consists of a experimental column 1 filled with a biosorbent. A 10.4 cm diameter glass column has been chosen. The column diameter allows evasion of the impact of a close-to-the-wall layer on the experimental tests. Glass walls allow seeing the obstruction of the filter charge with oil products. 10 and 20 cm thick charge of a biosorbent has been chosen for the experiment. The grate 2 that supports the charge has been produced of the steel sieve with 1 mm meshes. The sieve was additionally covered with anticorrosion cover. A tank 3 of supply of the water polluted with the oil products is a hermetically closed tank in which an even concentration of oil products is kept. The height of this tank might be changed in order to achieve a necessary pressure of the water being supplied. The height of the supplied polluted water is observed with the help of a rule attached to the stand 4. In order to secure an even pollution of the water being supply, a mixer 7 has been installed in the tank 3.

The polluted water is made ready for the experiment in 50 l recalculation tanks 5. A mixture of petrol and diesel (50 l of water, 1 l of petrol, and 2 l of diesel fuel) is used for pollution. A surplus amount of mixture is maintained in the tank in order to keep a constant concentration of oil products in the water. The performed experimental tests have revealed that a part of oil products that disperses in the water remains constant when the thickness of oil products in the tank is (5–10) mm. A hermetic re-circulation tank has a circulation pump 6 that supplies polluted water to a supply tank 3. A sample is taken in the tank 8 of filtered water for an analysis and the speed of filtration is being observed, m/h.

Experiments showed that biosorbent charge of 10 cm (filtration speed 2.5 m/h) has good filtration efficiency (97 %) till 6 h after filtration start. Charge of 20 cm has 96 % filtration efficiency till 24 h. This allows a presumption that the thickness of the filter charge is essentially important when designing oil product filters.

6. Numeral Modelling of Oil Product Sorption Process

The goal of this modelling is to apply a mathematical model VS2DTI of pollutant dispersion in porous medium for the process of oil product sorption.

Sorption of oil products by a biosorbent (peat-moss) from the water and soil surface, i.e a mathematical model of a fragment of a certain real situation is drawn and it simulates spill of oil products and collection of these pollutants (sorption) with a biosorbent. In order to evaluate precision of a computer model, dependences of oil product sorption on time, found out in an experimental way, were compared with the data of mathematical modelling.

Collection (sorption) of oil products (viscosity is close to that of petrol and diesel fuel) spilled from the soil by a biosorbent is being simulated.

Oil products spilled on the soil surface first of all migrate to a sorbent (oil product concentration in the soil does not change). 10 min. after sorption starts, a biosorbent is fully saturated and filtration of oil products into the soil starts. When sorbent gets fully saturated, the non-absorbed oil residue slowly soaks into the soil.

The following results have been obtained when oil product concentration in a biosorbent (g/cm^3) was translated into sorption (g of oil product / 1 g of sorbent).

Results of the model shows that after 30 s sorbent absorbed 3.64 g/g of oil product; after 1 min – 4.6 g/g; after 10 min – 6.68 g/g; after 20 min – 9.07 g/g; after 30 min – 9.07 g/g; after 60 min – 9.07 g/g.

Comparing models of the rate of oil product sorption (viscosity is close to that of petrol and diesel fuel) from water or soil surface, it is obvious that oil products are absorbed from the water surface at a slightly higher rate than from the soil surface. Similar situation would be observed under real conditions, as slower sorption of oil products from the soil surface would be conditioned by roughness of the soil surface and poorer contact of the sorbent with the oil product.

To evaluate the function of conformity of distribution of digital model data, a correlation coefficient is used.

Based on the available data it has been calculated that the correlation coefficient of modelling results and experimental data of diesel fuel sorption is 0.896, while that of modelling and experimental petrol sorption data is 0.998.

As the correlation coefficient in both cases is close to 1, it means that the conformity of modelling (theoretical) and experimental results is good.

7. Conclusions and Recommendations

1. It has been found out that biosorbents are the most promising material for oil product localisation. Biosorbents, produced of local raw materials, would protect the Lithuanian market from the imported ones. In order to choose the most appropriate raw material for the production of biosorbents, experimental tests of potential materials have been performed.
2. The list of references to the literature dealing with the materials that absorb oil products shows that the optimal sorbents must comply with the environmental requirements: they should be easily collected, cause no damage even when they remain in nature, they should be biodegradable, and have potential for utilisation.
3. Under conditions prevailing in Lithuania, the waste of wood processing, cellulose and paper industry, ash, the waste of metal etching process, also calcium hydrosilicates (as waste recycling products), local rocks, peat and moss could serve as such materials.
4. Experimental examination of three plant raw materials that are potentially appropriate for the production of biosorbents (peat-moss, reindeer moss, chaf-hards mixture) shows that peat-moss has the best properties of oil product sorption.
5. The experiments carried out with different fraction peat-moss (the average fraction size of (3–5) mm; 2 – peat-moss with the average fraction size up to 1 mm) show that the biosorbent of coarser fraction has better properties of oil product sorption off the water surface: on the average 25 % higher absorption of diesel and 22 % higher absorption of petrol, when compared with the moss of finer fraction.
6. In order to reduce the water sorption by peat-moss thermal modification is potentially appropriate. It has been found out that thermal modification of a biosorbent enables 6 time slower water absorption. The best temperature for the thermal modification is 225 ^{o}C. Heating duration is 60 min.

7. The temperature of 250 °C is critical for thermal modification of a biosorbent, as at this temperature disintegration of carbon combination and charring of a biosorbent starts.
8. The experimental tests have revealed that a biosorbent produced of local raw materials might be used a charge for the filter used for cleaning the water polluted with the oil products. Twice bigger thickness of the filter charge increases the maintenance period of the filter 4 times. This allows a presumption that the thickness of the filter charge is essentially important when designing oil product filters.
9. With the help of the VS2DTI software, a mathematical model of the speed of oil product sorption has been developed, which reflects a real intensity of the process of sorption of oil products by a biosorbent produced of peat-moss. The calculated correlation coefficient of modelling results and experimental data of diesel fuel sorption is 0.896, and that of modelling and experimental petrol sorption data is 0.998. This shows a good conformity of theoretical (modelled) and experimental data, thus the use of a computer-generated model would enable the expansion of the limits of peat-moss sorbent examinations.

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Patent

Baltrėnas, P.; Vaišis, V. Biosorbent (Biosorbentas): invention patent of the Republic of Lithuania. A patent application has been announced in the Newsletter No. 1 (2005) of the State Patent (patentinė paraiška paskelbta Valstybinio patentų biuro 2005 m. biuletenyje Nr. 1).

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NAFTOS PRODUKTUS SUGERIANČIŲ BIOSORBENTŲ TYRIMAS IR ĮVERTINIMAS

SANTRAUKA

Problema

Pagrindiniai gruntą teršiantys teršalai yra organiniai junginiai (nafta ir jos produktai, riebalai ir t. t.), metalų junginiai, buitinės atliekos. Buitinės atliekos bei riebalai, lyginant su nafta ir jos produktais, negausiai teršia gruntą. Be to, šie teršalai daugiausiai patenka iš buitinių nutekamųjų vandenų, kurie dažniausiai valomi. Todėl Lietuvoje šiuo metu didžiausias dėmesys skiriamas naftos ir jos produktų pašalinimui iš dirvožemio.

Tiesioginiais tyrimais šalyje jau išaiškinta daugiau kaip 300 žemės gelmių užteršimo naftos produktais vietų. Gruntas ir požeminis vanduo užterštas beveik visuose tyrinėtuose naftos produktų sandėliavimo ar realizavimo objektuose (naftos bazėse, degalinėse, katilinėse ir kt.), kurių Lietuvoje yra keletas tūkstančių.

Nafta ir jos produktais teršiamos jūros ir vandenynai. Jų taršą pagrindinai skatina naftos telkinių eksploatavimas, intensyvi laivyba, žaliavinės naftos bei jos produktų transportavimas.

Įvertinus pažeidimų mastą, pavojingumą ir taršos likvidavimo priemones bei kaštus, galima teigti, kad grunto teršimas naftos produktais yra aktuali ekologinė problema.

Darbo aktualumas

Patekus naftos produktams į aplinką visų pirma atliekama teršalų lokalizacija. Tam naudojami sorbentai. Todėl potencialios taršos naftos produktais vietose būtinos jų atsargos. Siekiant įvertinti šių medžiagų kiekio pakankamumą, būtini detalūs naftos produktų sorbcijos tyrimai. Be to, sorbentai turi atitikti aplinkosauginius reikalavimus: jie turi būti lengvai surenkami, kad net ir likę gamtoje nedarytų jai žalos, biodegraduojantys, su perspektyviomis utilizacijos galimybėmis. Būtent šiuos reikalavimus atitinka biosorbentai, kurie gaminami iš natūralių gamtinių išteklių.

Avarijų metu išsiliejusi nafta padaro didžiausią žalą aplinkai, todėl labai svarbu atlikti kompleksinius priemonių, skirtų taršos likvidacijai, tyrimus.

Darbo tikslas ir uždaviniai

Tikslas – atlikti kompleksinius naftos produktus sugeriančių biosorbentų tyrimus ir išanalizuoti sorbcijos procesą, panaudojant vietines žaliavas naftos produktų išsiliejimų likvidacijai. Darbo uždaviniai:

- įvertinti naftos produktų taršos likvidavimui naudojamų medžiagų sorbcines savybes;
- identifikuoti optimaliausią medžiagą sorbento gamybai iš vietinių žaliavų;
- atlikti kompleksinius eksperimentinius sorbcijos proceso tyrimus;
- nustatyti naftos produktų sorbentų fizikinius parametrus;
- atlikti eksperimentinius vandens įgerties tyrimus;
- atlikti sorbcijos efektyvumo nuo vandens paviršiaus tyrimus;
- nustatyti liekamąją sorbuojamos medžiagos dalį;
- atlikti pilnutinio sorbcijos talpumo eksperimentinius tyrimus;
- atlikti terminės biosorbentų modifikacijos tyrimus;

- nustatyti sorbento frakcijos įtaką sorbcinėms savybėms;
- atlikti užteršto vandens valymo biosorbentais eksperimentinius tyrimus;
- atlikti sorbcijos proceso matematinį modeliavimą.

Darbo naujumas

Darbo naujumą sudaro kompleksinis naftos produktų biosorbento tyrimas, apimantis teorinę sorbcijos proceso analizę, eksperimentus ir kompiuterinį modeliavimą. Darbe nagrinėjamos lietuviškų medžiagų panaudojimo galimybės biosorbentų gamybai.

Ginamieji disertacijos teiginiai

- iki šios Lietuvoje nėra atlikta kompleksinių naftos produktų biosorbentų tyrimų, apimančių sorbentų fizikinių charakteristikų, sorbcijos greičio nuo vandens, dirvožemio paviršių, vandens filtravimo eksperimentinius tyrimus bei sorbcijos proceso matematinį modeliavimą;
- biosorbentą galima gaminti iš Lietuvoje augančių samanų kiminų;
- samanų kiminų sorbentas gali būti naudojamas naftos produktų išsiliejimams likviduoti tiek nuo dirvožemio, tiek nuo vandens paviršių;
- biosorbentas gali būti naudojamas kaip vandens valymo filtrų įkrova;
- matematinio modeliavimo rezultatai patvirtina eksperimentų metu gautus rezultatus.

Darbo praktinė vertė

Atlikti eksperimentiniai tyrimai bei jų metu gauti rezultatai parodė, kad biosorbentas, gaminamas iš vietinių žaliavų, gali būti sėkmingai naudojamas likviduojant naftos produktų išsiliejimus. Biosorbentas sorbcinėmis savybėmis nenusileidžia pramoniniams sorbentams, be to, jis gali būti naudojamas kompleksiškai – surenkant naftos produktus nuo dirvožemio bei vandens paviršių ir naudojamas kaip užteršto vandens filtro įkrova.

Rezultatų aprobavimas

Doktorantas paskelbė 11 mokslinių publikacijų: 1 mokslinis straipsnis užsienio žurnale su ISI citavimo indeksu; 2 mokslo straipsniai užsienio žurnaluose; 3 mokslo straipsniai žurnaluose, įrašytuose į LL sąrašą; 5 mokslo straipsniai kitoje Lietuvos spaudoje.

Disertacijos rezultatai aptarti 3 tarptautinėse, 4 respublikinėse mokslinėse konferencijose bei išspausdintos 6 mokslinės publikacijos konferencijų pranešimų medžiagose.

Gautas teigiamas sprendimas Lietuvos respublikos išradimo patentui „Biosorbentas“ gauti. Patentinė paraiška paskelbta Valstybinio patentų biuro 2005 m. Nr. 1 biuletenyje.

Darbo apimtis ir struktūra

Disertaciją sudaro įvadas, 7 skyriai, bendrosios išvados, bendros literatūros, autoriaus publikacijų bei skaitytų pranešimų darbo tematika sąrašai. Darbo apimtis – 141 teksto puslapiai, 73 paveikslų, 4 lentelės.

Išvados ir rekomendacijos

1. Nustatyta, jog perspektyviausia naftos produktų lokalizacijos priemonė yra biosorbentai. Biosorbentai, gaminami iš vietinių žaliavų, apsaugotų Lietuvos rinką nuo įvežtinių.
2. Atlikus naftos produktus sorbuojančių medžiagų literatūros apžvalgą matyti, kad optimalus sorbentas turi atitikti aplinkosauginius reikalavimus: lengvai surenkami, net ir likę gamtoje nedarytų žalos jai, biodegratuojantys, su perspektyviom utilizacijos galimybėm.
3. Eksperimentiškai ištyrus tris augalines žaliavas, potencialiai tinkamas biosorbentų gamybai (samanų kiminai, elninė šiurė, spalių-pakulų mišinys), matyti, jog geriausiomis naftos produktų sorbcijos savybėmis pasižymi samanų kiminai.
4. Atlikti eksperimentai su skirtingų frakcijų samanų kiminais (vidutinis dalelių stambumas (3–5) mm bei dalelių stambumas iki 1 mm) rodo, kad stambesnės frakcijos biosorbentas pasižymi geresnėmis naftos produktų sorbcijos nuo vandens paviršiaus savybėmis: vidutiniškai 25 % didesnė dyzelinio kuro įgertis bei 22 % didesnė benzino įgertis lyginant su smulkesnės frakcijos samanomis.
5. Siekiant sumažinti samanų kiminų vandens įgertį, būtinas šios sorbuojančios medžiagos impregnavimas ar kitokio pobūdžio modifikavimas. Kaip potencialiai tinkamas išskirtas terminis modifikavimas.
6. Nustatyta, jog biosorbento terminė modifikacija leidžia sumažinti vandens įgeriamumą 6 kartus. Geriausiai tinkama temperatūra terminei modifikacijai yra 225 ^{o}C. Kaitinimo trukmė 60 min.
7. 250 ^{o}C temperatūra yra kritinė termiškai modifikuojant biosorbentą, nes prie šios temperatūros skyla anglies jungtys ir biosorbentas pradeda anglėti.
8. Eksperimentiniai tyrimai parodė, kad biosorbentas iš vietinių žaliavų gali būti naudojamas kaip naftos produktais užteršto vandens valymo filtro užpildas. Dvigubai padidinus filtro įkrovos storį filtro eksploatacinis

laikas padidėjo 4 kartus. Tai leidžia daryti prielaidą, jog filtrinio užpildo storis yra itin svarbus projektuojant naftos produktų filtrus.

9. Remiantis VS2DTI kompiuterine programa sukurtas naftos produktų sorbcijos greičio matematinis modelis atspindi realų samanų kiminų biosorbento naftos produktų sorbcijos proceso intensyvumą. Aukštas koreliacijos koeficientas rodo gerą teorinių (modeliavimo) ir eksperimentinių duomenų atitikimą, todėl sukurto kompiuterinio modelio panaudojimas leistų išplėsti samanų kiminų sorbento taikymo galimybių ribas.

Trumpos žinios apie autorių

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Vaidotas Vaišis

INVESTIGATION AND EVALUATION OF BIOSORBENTS FOR OIL PRODUCTS

Summary of Doctoral Dissertation
Technology Sciences, Environmental Engineering and Landscape Management (04T)

Vaidotas Vaišis

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