Earth Systems and Environment
https://doi.org/10.1007/s41748-018-0048-8

ORIGINAL ARTICLE

Non-woven Textile Materials from Waste Fibers for Cleanup of Waters Polluted with Petroleum and Oil Products

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Received: 27 January 2018 / Accepted: 10 April 2018

Abstract
The aim of this work was to investigate the possibility of using non-woven materials (NWM) from waste fibers for oil spill cleanup and their subsequent recovery. Manufacture of textile and readymade products generates a significant amount of solid waste. A major part of it is deposited in landfills or disposed of uncontrollably. This slowly degradable waste causes environmental problems. In the present study are used two types of NWM obtained by methods where waste fibers are utilized. Thus, real textile products are produced (blankets) with which spills are covered and removed by adsorption. These products are produced by two methods: the strengthening of the covering from recovered fibers is made by entanglement when needles of special design pass through layers (needle-punching) or by stitching with thread (technology Maliwatt). Regardless of the random nature of the fiber mixture, the investigated products are good adsorbents of petroleum products. The nature of their structure (a significant void volume and developed surface) leads to a rapid recovery of the spilled petroleum products without sinking of the fiber layer for the sampled times. The used NWM can be burned under special conditions.

Keywords Non-woven materials · Oil pollution · Textile waste · Adsorption

1 Introduction

Hydrocarbons come into the aquatic environment from a variety of natural and artificial sources. Maritime transport contributes to this utmost. Most of the oil emission are caused by floating of vessels, and smaller part of incidents. When oil is spilled on the water surface, it disperses rapidly and after a few hours the stain typically begins to break apart and form narrow sectors parallel to the wind direction. Consequently, the oil will be dispersed over a huge area with large differences in thickness of the floating layer in a short time. When oil contacts water, a layer (oil film) is formed on the surface which breaks the exchange of energy between the atmosphere and the seawater. Its low surface tension, low gas permeability and other negative qualities adversely affect the water physical and chemical conditions. Incoming volatile petroleum products and medium and heavy distillate fractions lead to flora and fauna destruction in the sea basin, as these carcinogenic hydrocarbons subsequently enter the human body with the consumed food (Dobrevski et al. 1987; Elhag and Bahtawi 2016).

There are several methods which can help in limiting the damage from the spill and oil to be cleaned. The most commonly used techniques include collection and recovery,

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Published online: 19 April 2018

dispersion, bio-processing and incineration (ITOPF; White 2000; Baird 2008).

Sorbent materials are widely used for collecting and completely removing spilled oil products. Placing the sorbents in the spill facilitates the change from liquid to semi-solid phase and hence oil removal together with the sorbent is much easier. Good sorbents have hydrophobic and oleophilic properties, high degree of absorption and retention for a long period of time on the surface of the water, allow the extraction of oil and finally enable absorbed oil to be reused or recycled (Adebajo et al. 2003). Sorbents can be used in turbulent or fast-flowing water and also in difficult to access places, such as coasts, where it is impossible to use defractors or vacuum devices and can serve as enclosures (sorbent booms) (Baird 2008).

Sorbents absorb oil through the mechanisms of absorption or adsorption and, because they have a certain porosity, oil is collected by capillary action. Often, both the techniques—collection and sorption—are combined (Aboul-Gheit et al. 2006). Adsorption of aqueous solutions is carried out as a result of the gradual increase in the concentration of substances on the surface of the adsorbent. The degree of retention of certain components is determined by the difference in the energy of the interaction of the adsorbent with the molecules of water (hydration) and the extractive matter (Elhag et al. 2017).

Sorbents of petroleum products include a very wide variety of organic, inorganic and polymeric substances designed to remove oil and petroleum products, mainly from water. Their composition and characteristics depend on the material used and the assumed use in oil spillage. Fibrous materials (FM) are highly efficient against oil outflow when they are used to collect oil and oil products (OP) from the water surface. It is most promising to use various FM (hydrophobized, additionally treated with an active substance) in the form of mats, multilayer units and non-wovens. These sorbents may be used many times and recovered at the site by mechanical streaking, treating with solvents, live stream, etc. They are often based on natural fibers, either plant based (cotton, flax, hemp) or mineral ones (asbestos) (Khlestkin and Samoilov 2000; Pat. 2097125 RF 1997; Pat. 2197321 RF 2003).

There are sorbents composed of a fibrous cellulose material in the form of technological wool or wastes of textile works (93–97 mass %) treated with oxidized ataxic polypropylene (Sirotkina and Novoselova 2005) or a block copolymer of butadiene and 10–50% styrene (2–10 mass %) (Pat. 2097125 RF 1997). The advantages of these materials are high sorption capacity with respect to oil (up to 30 g g^{-1}) and the ability to survive many recovery cycles, which ensures multiple use of these materials. A shortcoming is the trend is being prone to microbiological decomposition. NWM made from recycled knitted sweaters with composition viscose/polyethylene 78/22 is proposed for the collection by sorption of crude oil, diesel fuel and vegetable oil (Radetic et al. 2008).

Non-woven materials (NWM) have an ever-wider application in environmental protection because the technologies for their production are highly productive and allow the use of non-standard, waste and recovered fibers. They have good physico-mechanical performance, in some cases superior to those of classic textiles, and the respective technologies enable the production of a finished product with specific properties and non-standard application.

Needle punching is the oldest process for the preparation of non-wovens. In this process, the fibers are transferred into the depth of the wadding by needles with special design and are intertwined. Thus, a product is yielded with a three-dimensional structure, with high density and durability and resistance to mechanical impact, which is a prerequisite for its widespread use for household and technical purposes (Kamath et al. 2004).

Stitch bonding is a method for NWM production using mainly cross-laid and air-laid batts as the batt passes between the needles and the guide bar. A warp knitting is carried out resulting in overlaps on the one and underlaps on the other side of the batt (Horrocks and Anand 2000).

Physical–mechanical properties depend significantly on machine-technical parameters of the process and can be easily controlled. These are two of the most common methods of using the fiber waste from the stages of producing yarn in the production of clothing and its recycling after use. The composition of this waste consists of natural and chemical fibers such as cotton, viscose, polyester, polyacrylonitrile, polyamide and polypropylene. The main raw material for the production of synthetic fibers is petroleum. Even the production of natural polymers such as cotton requires energy and chemicals based on non-renewable resources. Using non-woven materials allows the control of bulk density, free volume and hence the rate of sorption from the material. This is an advantage compared with bulk sorbents—the most commonly used carbon sorbents, especially activated charcoal with developed porosity. Of the fibrous materials, the most widely used for this purpose are polypropylene fibers (which are present in the mixture we use) and needle-punched materials with different thicknesses (Kulikova 2008).

The aim of this work is to investigate the possibility of using non-woven materials with different compositions from waste fibers for oil spill cleanup and their calorific value after combustion.

2 Materials and Methods

Seawater differs from freshwater in the content of dissolved ions. Water in the world's oceans has an average salinity around 3.5%. Due to the added weight of the salts, the relative weight of seawater at the ocean surface is 1.025 g ml^{-1}, while freshwater reaches a maximum of 1000 g ml^{-1}.

NWM, obtained by needle-punching and stitch-bonding method (Fig. 1), with parameters listed in Table 1 and a size of 5×5 cm, were used.

The physico-mechanical parameters depend significantly on the mechanical and technical characteristics: the degree of fineness, the sewing step, the type of the knitting, as well as the technological factors—the mass and type of the wool and the type of sewing thread.

For the experimental work, we used seawater taken from the Black Sea in the Bourgas area. Two types of oil were used—mineral motor oil OMV Austroil SAE 15 W/40 and waste motor oil collected from an oil change workshop. A methodology was developed in a laboratory using different amounts of pure mineral and waste oil in static conditions and agitation and residence time of the samples in the suspension from 10 to 30 min in beakers of 600 ml in which were placed 100 ml of seawater and 2 ml oil. The degree of sinking was determined after a period of 48 h. Five parallel studies were performed for each sample, the obtained results were averaged and a statistical analysis was performed using ANOVA Single Factor program. The evaluation was done using the Fisher criterion by comparing its estimated value (F_R) with the table value (F_T). If $F_R > F_T$, it is assumed that the factor affects the property tested, and if $F_R \leq F_T$ it does not affect the results of the study. The operating conditions are listed in Table 2.

The used materials were characterized by determining the thickness, volume density, mass per unit area and air permeability. Retention and extraction of oil from the suspension were determined by weight after drying for 4 h at 105 °C with blasting.

Fig. 1 Photos of the materials used

Table 1 Used materials

Materials	Type	Composition	Parameters
Material 1	Stitch-bonding type Maliwatt	Wool 15% Cotton 18% Viscose 20% Polyester 17% PAN 30% Stitch fiber–polyester 100%	Step of stitching: 2.12 cm Length of thread in 1 cm: 3.74 cm Number of stitches in 1 cm: 3.2
Material 2	Stitch-bonding type Maliwatt	Wool 5% Cotton 20% Viscose 17% Polyester 23% PAN 35% Stitch fiber–polyester 100%	Step of stitching: 0.7 cm Length of thread in 1 cm: 3.26 cm Number of stitches in 1 cm: 3
Material 3	Needle punched	Wool 20% Cotton 20% Viscose 20% Polyester 20% PAN 15% Polyamide 5%	Frequency of needle-punching: 500 min^{-1} Depth of needle-punching: 12 mm Projection density: 15 needles cm^{-1}
Material 4	Needle punched	100% recovered wool	Frequency of needle-punching: 800 min^{-1} Depth of needle-punching: 10 mm Projection density: 50 needles cm^{-1}

Table 2 Operating conditions

Stage	Time, min
Agitation (if applied)	2
Stay of the water and oil suspension after agitation (if applied)	10
Sample stay in the water and oil suspension	10, 20 or 30
Sample storage after removal from water	10
Drying	120
Storage after drying	10

3 Results and Discussion

Figure 2 shows scanning electron microscopy (SEM) images of Material 1 (mixed composition) and Material 4 (with oil pollution) as both NWM are obtained from recycled clothing.

Used stitch-bonded materials (Material 1 and 2) have a smaller thickness, and needle-punched materials (Material 3 and 4), particularly from recovered wool, have a greater thickness (Fig. 3).

Stitch-bonded materials on the other hand are more voluminous and porous, with a large amount of open pores due to insufficient entanglement of the fibers in the volume of the product (Fig. 4).

Results in terms of mass per unit area in the samples indicate that the amount of fibers in the needle-punched samples is greater; therefore, they have more developed fibrous surface as a result of which a greater sorption capacity can be expected (Fig. 5).

The results for air permeability that show the porosity and free volume of the device and the included air in it indirectly indicate the ability of the product to be retained on the surface of the water and to sorb as long as possible the contamination as in Material 4 (100% recovered wool), which has the highest coefficient (Fig. 6).

Statistical analyses showed that the rate of uptake of oil by the fibrous sorbents depends on the type of non-woven material, its composition, and also on the conditions of the experiment—under static conditions or agitation, the type of pollutant itself and clean motor or waste oil with p values < 0.05 (Figs. 7, 8). The rate of uptake does not depend on the residence time of the material in the suspension regarding the type of oil used (clean or waste) or the condition (under static conditions or agitation). It is only observed that increasing the time from 10 to 30 min affects the holding capacity of Material 3 of waste oil with agitation ($p = 0.008775$).

It was found that the amount of sorbed pollutant under dynamic conditions is less (Fig. 8) than under static conditions. Stitch-bonded products adsorb a larger amount of pollutant, due to the large volume and mixed composition.

In this case, stitch-bonded Material 2 showed better ability to adsorb waste oil working with or without agitation, but the trend for greater efficiency of the sorbent under static conditions remained the same. This is shown in Fig. 9, wherein the samples remained in the suspension.

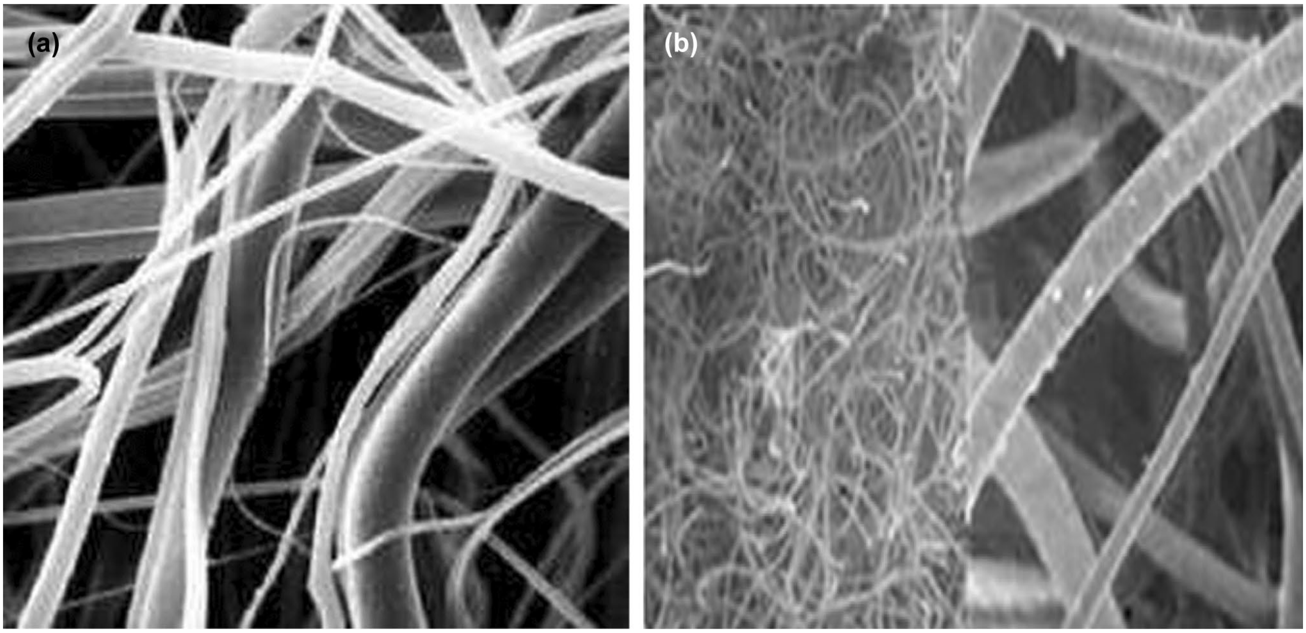

Fig. 2 SEM images of Material 1 ×100 (**a**) and Material 4 with oil pollution ×600 (**b**) showing the nonwoven texture

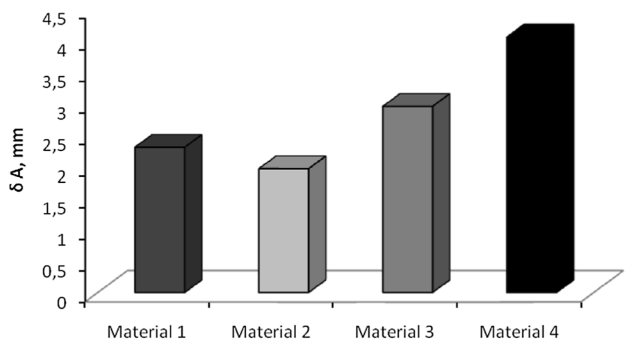

Fig. 3 Thickness of the used fibrous sorbents

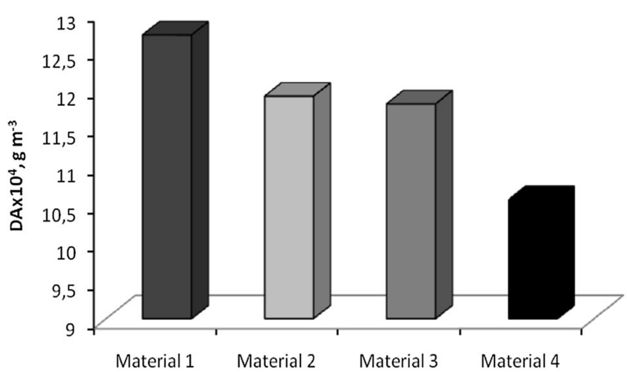

Fig. 4 Volume density of the used nonwoven samples

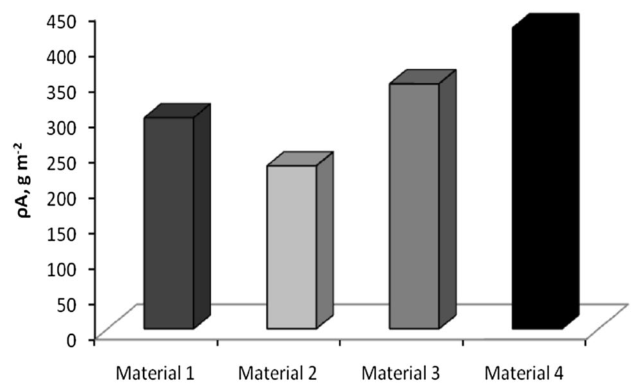

Fig. 5 Mass per unit area of the used nonwoven samples

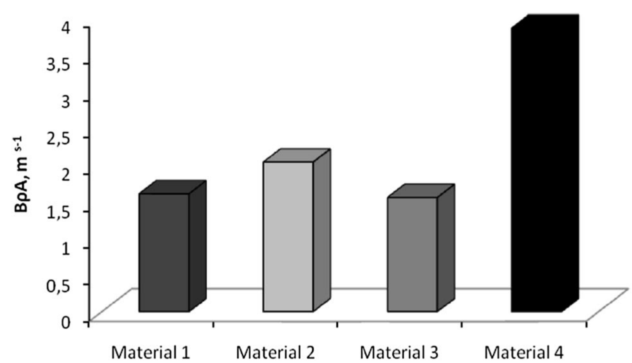

Fig. 6 Coefficient of air permeability of used nonwoven samples

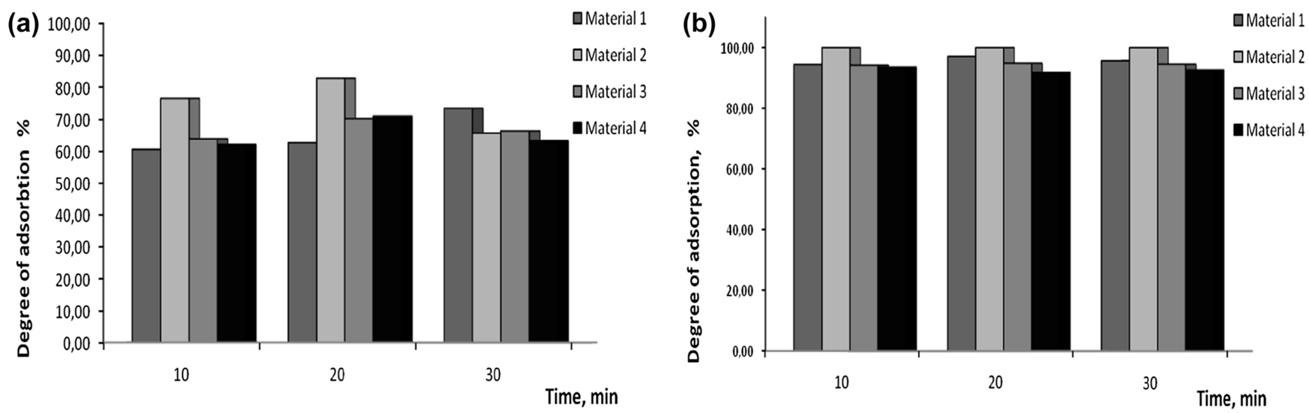

Fig. 7 Degree of adsorption of pure oil under agitation (**a**) and under static conditions (**b**) depending on the residence time of the sample in suspension

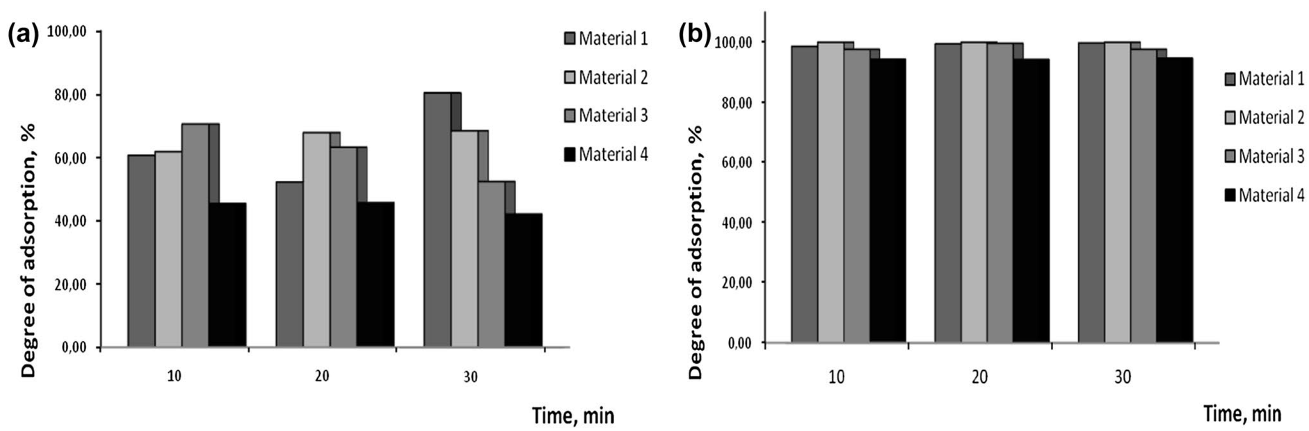

Fig. 8 Degree of adsorption of waste oil under agitation (**a**) and under static conditions (**b**) depending on the residence time of the sample in suspension

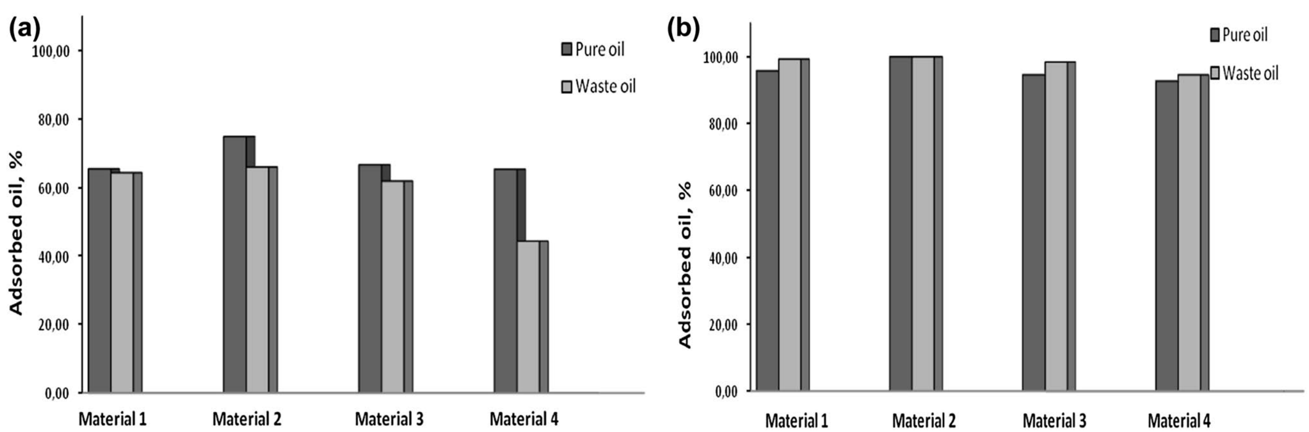

Fig. 9 Adsorbed pollutant under agitation (**a**) and under static conditions (**b**) according to its type

Generally, materials showed better ability to retain pure oil under agitation and waste oil under static conditions. Stitch-bonded materials are effective sorbents whatever the conditions of the experiment. Based on all conducted analyses, Material 2 (stitch-bonded type Maliwatt with a composition of wool 5%, cotton 20%, viscose 17%, polyester 23%, PAN 35%, stitch fiber–polyester 100%) was most effective at the tested conditions, probably due to the reduced content of hydrophilic fibers in the mixture and the larger content of PAN and PET (Fig. 10). Samples with the lowest bulk density retain a small amount of oil, due to the presence of air in the pore volume, which impedes the penetration of the suspension into the volume of the fibrous sorbent. This is confirmed by the results obtained for air permeability—samples with the highest coefficient of air permeability absorb the least amount of oil products.

The statistical analysis showed that changing the amount of oil does not affect the ability of the material to retain pure oil ($F_R = 2.28 < 5.14 = F_T$).

In the determination of buoyancy during the preliminary investigations, it was found that the tested materials remained on the surface of the fluid for over 48 h, from which it can be concluded that they have good buoyancy and provide sufficient time for completion of all scrubbing operations and collection of the blanket of NWM.

On the other hand, retention of the material on the surface of the suspension and its sinking depend precisely on the enclosed air in the system. At this stage of the study, samples of any kind do not sink after a stay in static and dynamic conditions after 48 h. In addition to the wetting characteristic, the capillarity of the sorbable substance itself plays an important role, and the rate and the sorption capacity is directly related to the available sorbent area. There is a large contact between the sorbent and sorbate in the materials studied due to the high volume of non-woven fabric and the developed surface of the individual fibers.

There are fibrous materials available in the form of mats and blankets that are placed on the polluted surface and the sorbed petroleum products and oil can be mechanically squeezed. These adsorbents can be used repeatedly, up to 14 times (Kończewicz et al. 2015), but unlike the material proposed by us, they are produced only of polypropylene which is not a waste product.

An analysis of the calorific value of different materials after saturation was provided in a certified laboratory. The test was performed according to BSS ISO 1928. The obtained results are presented in Table 3.

After use of the sorbents, their calorific value increases and therefore can be used as an energy source. But due to the change in the code of the waste (according to the EU legislation), they have to be burned in special facilities such as tunnel kilns.

Table 3 Results from combustion of waste samples

Material	Heat of combustion, kcal kg^{-1}	
	Unprocessed material	Processed material
Material 1	5754 ± 30	30 015 ± 30
Material 2	7399 ± 30	31 452 ± 30
Material 3	7260 ± 30	31 361 ± 30
Material 4	8122 ± 30	34 365 ± 30

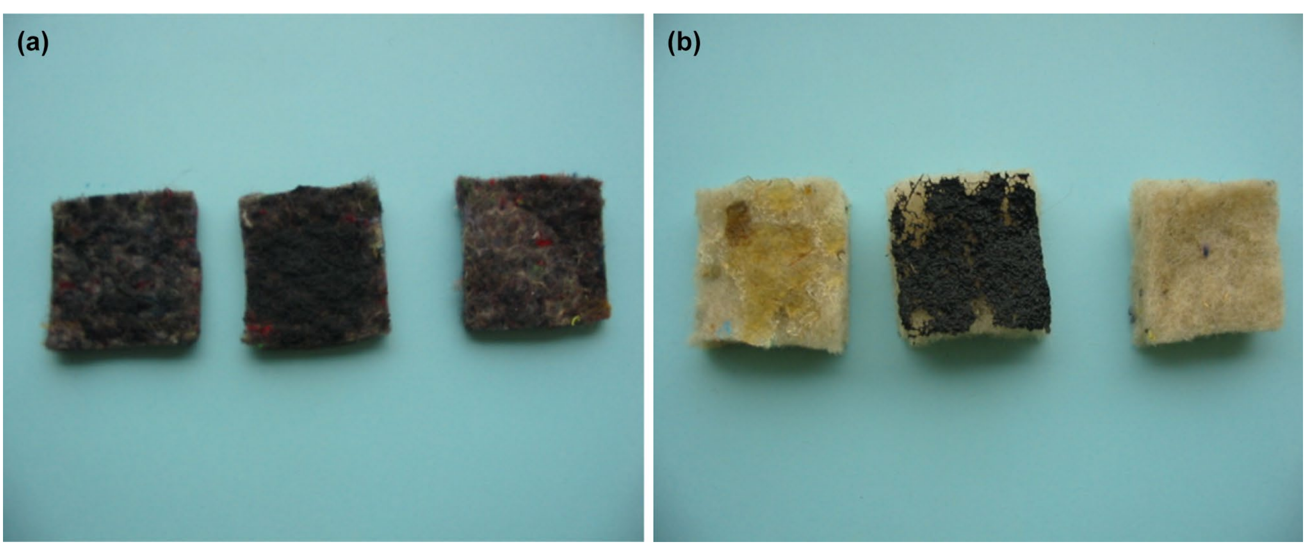

Fig. 10 Photos of Materials 1–3 (**a**) and Material 4 (**b**) tested after 48 h on the surface of contaminated water in static conditions. For the period of time, the textile adsorber remained on the surface

4 Conclusions

As a result of tests carried out, it has been found that the stitch-bonded non-woven materials have better ability to retain oil in comparison to needle-punched material, because of the greater amount of free fibrous surface. The use of waste fiber mixtures with a higher content of PAN is more effective for absorbents of petroleum. The oil capacity of the material is characterized by oil sorption in the static and the dynamic regime. In addition, it should be noted that there is a possibility of modifying the materials additionally to enhance the existing properties or to render new ones. Such an approach in general allows one to develop new purification technologies in which a large number of materials are characterized by good efficiency. Textile sorbents sink after different periods of stay in the water depending on the amount of hydrophilic fibers in their composition, but these studies continue in order to provide prescription for the way time of use of non-woven blankets from regenerated fibers. The materials surveyed remain on the surface of the water under static conditions and agitation, not sinking even after 48 h stay. Their reuse and biodegradability make them a good alternative to existing synthetic sorbents. The aim and effects of their implementation are considered to be entirely positive—on the one hand, the use of waste products for NWM and, on the other hand, the removal of oil and petroleum products from polluted waters. The obtained sorbents can be used in petrochemical and oil industry and for wastewater treatment from petroleum products. This study reveals that non-woven fabric with mixed composition is an efficient, economic and eco-friendly oil adsorbent for oil removal from the surface of water.

Acknowledgements The project no. BG161PO003-1.1.05–0261/15.02.2013 "Filter media of non-wovens", developed by E-SOLAR Ltd., was funded under the Operational Program "Development of the Competitiveness of Bulgarian Economy" 2007–2013 and co-financed by the European Union through the European Regional Development Fund and the national budget of the Republic of Bulgaria.

Compliance with ethical standards

Conflict of interest On behalf of all the authors, the corresponding author states that there is no conflict of interest.

References

Aboul-Gheit AK, Khalil FH, Abdel-Moghny T (2006) Adsorption of spilled oil from seawater by waste plastic. Oil Gas Sci Technol Rev IFP 61:259–268. https://doi.org/10.2516/ogst:2006019x

Adebajo MO, Frost RL, Kloprogge JT, Carmody O (2003) Porous materials for oil spill cleanup: a review of synthesis and absorbing properties. J Porous Mater 10:159–170. https://doi.org/10.1023/A:1027484117065

Baird S (2008) Environmental costs of energy use. Oil Spills. http://www.spec.bc.ca/textfiles/Oil%20Spills.pdf. Accessed 4 May 2016

Dobrevski I, Mavrov V, Nenov V, Ganev V (1987) Technology of water—part II. Technika, Sofia **(in Bulgarian)**

Elhag M, Bahtawi J (2016) Consideration of geo-statistical analysis in soil pollution assessment caused by leachate breakout in the municipality of Thermi, Greece. Desalin Water Treat 57:27879–27889. https://doi.org/10.1080/19443994.2016.1168583

Elhag M, Bahrawi J, Galal HK, Aldhebiani A, Al-Ghamdi AAM (2017) Stream network pollution by olive oil wastewater risk assessment in Crete, Greece. Environ Earth Sci 76:278. https://doi.org/10.1007/s12665-017-6592-y

Horrocks AR, Anand SC (2000) Handbook of technical textiles. Woodhead Publishing Ltd

International Tanker Owners Pollution Federation (ITOPF) http://www.itopf.com/. Accessed 3 Mar 2018

Kamath MG, Dahiya A, Hegde RR (2004) Needle punched nonwovens. Textiles Introduction 25

Khlestkin RN, Samoilov NA (2000) Mat. 4 Mezhdunar. konf. "Khimiya nefti i gaza", vol 2. STT, Tomsk, pp 191

Kończewicz W, Otremba Z, Sałek K, Walaszkowska N (2015) Comparison of nonwoven fabrics in terms of usefulness for oil spill combat. J KONES. Powertrain and Transport 22(3):99–103. https://doi.org/10.5604/12314005.1165978

Kulikova IY (2008) Modern technologies of cleaning soil territories and water areas from oil pollution. Environ Protecti Oil Gas Complex 25:72–75 **(in Russian)**

Pat. 2097125 RF (1997)

Pat. 2197321 RF (2003)

Radetic M, Ilic V, Radojevic D, Miladinovic R, Jocic D, Jovancic P (2008) Efficiency of recycled wool-based nonwoven material for the removal of oils from water. Chemosphere 70:525–530. https://doi.org/10.1016/j.chemosphere.2007.07.005

Sirotkina EE, Novoselova LYU (2005) Materials for adsorption purification of water from petroleum and oil products. Chem Sust Dev 13:359–375

White IC (2000) Oil spill response–experience, trends and challenges—8th international spill conference, 15–17 august 2000. Darwin, Australia