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Preliminary identification studies of a new eco-friendly and natural sorbent material

Apetroaei MR[1*], Nicolae FM[2], Atodiresei D[3], Cotorcea A[4], Pocora A[5], Cristea O[6], Mihalcea, A[7], Diaconu S[8]

[1] PhD. Eng., “Mircea cel Bătrân” Naval Academy, Dept. of Naval and Port Engineering and Management, Constanta, Romania, (manuela.apetroaei@anmb.ro).
[2] Professor, PhD Eng., “Mircea cel Bătrân” Naval Academy, Constanta, Dept. of Naval and Port Engineering and Management, Romania, (florin.nicolae@anmb.ro
[3]. Associate professor PhD Eng., “Mircea cel Bătrân” Naval Academy, Constanta, Romania, (dinu.atodiresei@anmb.ro).
[4] Associate professor PhD Eng, “Mircea cel Bătrân” Naval Academy, Dept. of Naval and Port Engineering and Management, Constanta, Romania, (alexandru.cotorcea@anmb.ro).
[5]) Assistant professor, Ph.D std. Eng, "Mircea cel Batran” Naval Academy, Dept of Navigation and Naval Transport, Constanta, Romania, (andrei.pocora@anmb.ro).
[6] PhD Eng., “Mircea cel Bătrân” Naval Academy, Department of Tactics and Naval Armament, Constanta, Romania, (ovidiu.cristea@anmb.ro).
[7] Student, “Mircea cel Bătrân” Naval Academy, Dept of Naval and Port Engineering and Management, Constanta, Romania, (anca.mihalcea.11@gmail.com).
[8]Coremar, Constanta Port, Dana 0, Constanța, Romania

Abstract. Maritime transport is associated with the generation of various types of pollution, especially accidental oil spills, which have priority both perceptually and quantitatively. Due to their negative impact on marine ecosystems, these spills have become a major concern for both researchers and society. Also, this concern exists on the Romanian Black Sea coast, where chemical pollution could be a serious risk to the biodiversity and productivity of the marine ecosystem. As a result, several regulations, methods, and technical ways have been developed to mitigate and prevent this environmental problem.
Additionally, clean-up efforts that may have a direct impact on marine environments should not be disregarded. Thus, it is critical that toxins are removed from the environment promptly and efficiently, and the use of natural absorbent, biodegradable, non-toxic, and ecologically friendly materials is encouraged.
The aim of our preliminary study is to identify a new absorbent, biodegradable material based on a plant that is found in abundance in nature (Lythrum Salicaria) with a possible decontamination potential comparable to that of a natural, standardized material currently used successfully in the clean-up of petroleum products (Spill-Sorb).
Therefore, comparative studies have been carried out both to improve the hydrophobicity and to measure the absorption capacity of the powder associated with the aerial parts and, respectively, the roots of *Lythrum salicaria*, as potential sorbent materials for the oil field.
Key words: *oil pollution, natural sorbent material, hydrophobicity, absorption capacity*

1. Introduction

Nowadays, pollution from shipping is a reality, despite the MARPOL Convention's (Annex I) regulations addressing oil pollution from ships [1], as well as research assessing the risks presented by prospective oil spills along coastlines [2]. According to published data, around 20 % of total marine pollution is attributed to ship accidents and everyday operations, whereas 80 % is attributed to ship operating spills, such as waste oil spills or tank cleaning operations [3]. Additionally, the type of petroleum products used (diesel oil or heating oil) or transported (refined or crude oil) in maritime transport is largely determined by their chemical composition (polycyclic aromatic hydrocarbons) and physical-chemical properties: density, low solubility, rapid spread in a large mass of water, low vapor pressure, bioaccumulation, oxidation, and emulsification, among others. The majority of them impacted negatively on the environment, society, and economy as a result of the PAHs' mutagenic and carcinogenic characteristics [4].

As a result, there is a growing emphasis on developing novel alternative technologies for removing oil and oil product pollutants, which can have a negative impact on human health and cause significant damage to the marine environment. Among all the available technologies for removing oil products from the environment, the use of plant-based bio-sorbents is regarded as the most advantageous option, both economically and environmentally. Hydrophobicity is a key property of biosorbents that is influenced by the chemical composition of the structure, the amount of surface wax, the physical configuration of the fibers, the twists and crimps, the surface roughness, and the porosity [5]. Additionally, the physical-chemical features of the oil or oil-derived products, such as density, concentration, and temperature, can affect the capacity for absorption [6]. The hydrophobicity of sorbents can be increased through physical and chemical processes. Their purpose is to act on cellulosic active functional groups, specifically the OH groups (from the -D glucopyranose unit), through a wide range of chemical reactions (esterification, etherification, halogenation, oxidation, alkalinization, mercerization, acetylation, benzoylation, etc.) or physical treatments, in order to rapidly and efficiently remove contaminants from the environment [5].

The purpose of this preliminary study is to identify a new absorbent, biodegradable, eco-friendly, and low-cost material based on a plant (aerial parts and roots) widely available in nature (*Lythrum Salicaria*), with the potential for decontamination, and to improve its hydrophobicity through the use of hot water treatment [5]. The results were compared to those obtained using a natural, standardized substance [7] developed in Canada and presently being utilized successfully in petroleum product cleanup (Spill-Sorb).

Lythrum salicaria, an invasive plant that develops in the sand and humid environs of Dobrogea, is a familiar sight. In traditional medicine, purple loosestrife is the most often used herb. Its aerial parts are used to cure a variety of conditions, including colds, eczema, varicose veins, and hemorrhoids [8, 9]. Due to its affinity for marshy and sandy soils, as well as its chemical composition, which is rich in hydrophilic and hydrophobic compounds [1], it has aroused our interest as a potential crude oil removal plant material.

2. Materials and Methods

Lythrum salicaria was collected from the Constanta North area (fig.1a), dried and stored under optimal temperature and humidity conditions. The aerial parts (fig. 1b) and roots (fig. 1c) have been separated and grinded to be processed individually. In order to identify which parts of the plant could be used as absorbent material (due to different chemical composition), both aerial parts and roots were immersed separately in distilled water at 80 °C, in a ratio of w/v = 1:20. For one hour, the samples were stirred (400 rpm) at a high temperature (80 °C).

Figure1 a. *Lythrum salicaria (Ls)*

Figure 1 b. Dried aerial parts

Figure 1 c. Dried roots

The aqueous suspensions were cooled, filtered, and the wet precipitates were oven-dried at 110 °C for 24 h.

In the study, five types of powders were analyzed and tested: untreated aerial plant *Ls* powder, treated aerial plant Ls powder, untreated root *Ls* powder, treated root *Ls* powder, and Spill Sorb powder (Fig.1 a).

The bulk density is an important physical-chemical feature in plant powder characterization and represents the ratio between the mass of an untapped chitosan sample and its volume, expressed in grams (g) per cubic centimeters (cm3) [10].

The bulk density of a powder is stated by the untapped bulk density type – dv (Eq. 1), and the measurements were carried-out in duplicate.

$$d_v = \frac{m_v}{V} \quad (1)$$

where:

dv - bulk density, expressed in g/cm^3

mv – mass of bulk powder, (g),

v – volume of the measured bulk powder mass, (cm^3).

Moisture content is determined by applying a thermogravimetric method, i.e., by loss on drying, in which the sample is heated and the weight loss due to evaporation of moisture is recorded. The moisture (M) of all the samples kept in atmospheric conditions was determined according to the AOAC 2000 standard [11] at 105 ± 1 °C using the equation (2), and the measurements were carried out in duplicate.

$$M\,(\%) = \frac{w_i - w_f}{w_i} \times 100 \quad (2)$$

where:
w_i = sample weight before drying (g);
w_f = sample weight after drying (g).

In order to find out if the hydrophobicity of modified sorbents was improved, an oil sorption capacity test was carried out according to the Standard Test Method for Sorbent Performance of Adsorbents (ASTM F726-12) [12] and the Anuzyte & Vaisis (2018) study [5].

In our study, a small quantity (0.5 g) of each powder subjected to being analyzed was packed inside a wire-mesh basket and immersed inside a beaker filled with liquid (Fig. 2(a)). In the oil sorption capacity test, the beaker was filled with 80 ml of tap water and 8 ml of crude oil was poured on top. Such a quantity of crude oil was chosen based on the sorbent height so that the entire area of the powder sorbent surface was accessible to the oil (Fig 2 b). Each mesh with the sorbent powder was taken out of the beaker after 1 h. The excess liquid was removed by keeping the mesh with the sorbent powder for 1 min above the beaker (Fig. 2(c)). The experiments were repeated twice.

An oil absorption test was conducted at the ambient room temperature (23 ± 2 °C). For oil sorption, REBCO crude oil was used. The physical-chemical properties of crude oil are as follows - density at 15 °C: 0.882 g/cm^3 and viscosity: 12-20 mm^2/s.

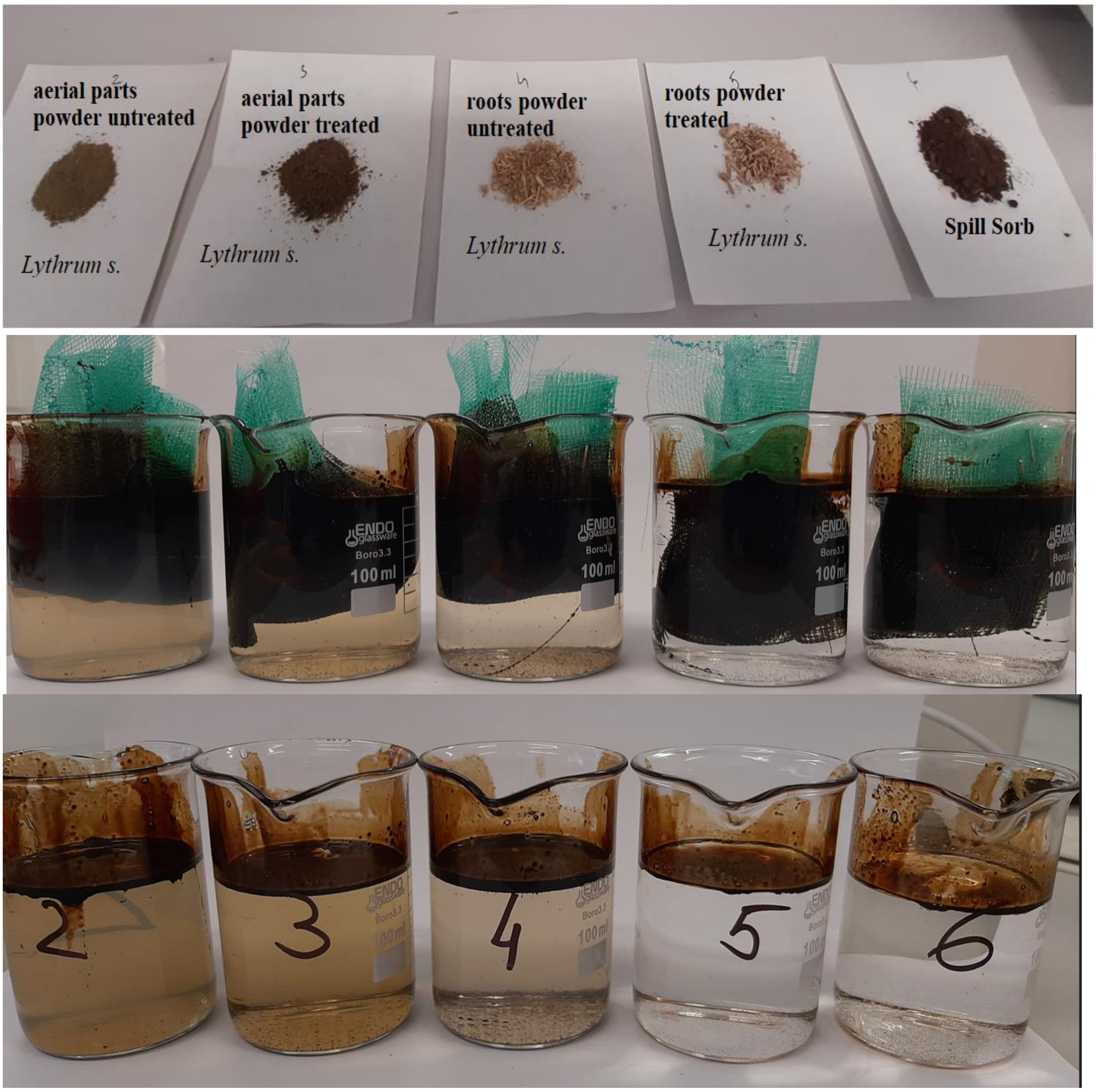

Figure 2. Oil sorption test: (**a**) powder samples tested; (**b**) beakers filled with crude oil and sorbent powder with the mesh; (**c**) crude oil excess elimination

The oil absorption capacity is calculated by applying equation (3):

$$M_{Oil} = \frac{(M_1 - M_2)}{M_S} \qquad (3)$$

where

M_{Oil} liquid absorption, g/g;
M_1 weight of the beaker with the liquid before the mesh with sorbent immersion, g;
M_2 weight of the beaker with the liquid after the mesh with sorbent immersion, g;
M_S weight of the sorbent powder, g.

3. Results and discussion

From the results of our study, it can be seen that the bulk density value of the tested powders is very important in characterizing the absorption process. According to the studies of Wong et al., (2016), the adsorption capacity of the contaminant is given by its dissipation in the mass of the plant powder [13]. But also, the physicochemical characteristics of the absorbed contaminant (density and viscosity) cannot be omitted either. In Fig. 3, it can be seen that the bulk density values of the treated powders (both aerial parts and roots of *Lithrum s.)* are close to the bulk density value of the Spill sorb powder.

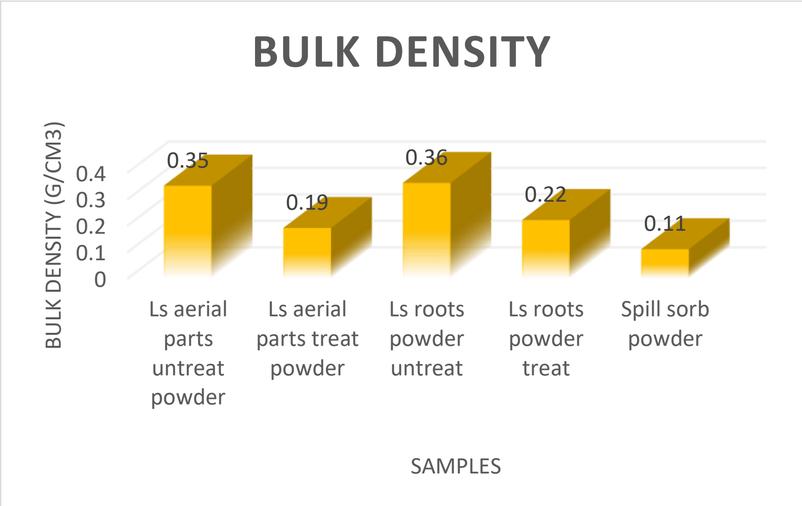

Figure 3. Bulk density of samples analyzed

Generally, the powder characteristics, such as morphology, size, size distribution, density, and surface area, could influence the contaminant absorption capacity as well as the moisture absorption capacity.

Moisture content can be defined on the basis of the change in capacitance or resistivity of the dielectric properties of a material before and after drying. Because vegetable powders, in general, are hygroscopic, this would negatively influence their flow, as they can be exposed to moisture during both storage and handling.

The similarity in terms of absorption between the *Lithrum s*. root treated powder sample and the Spill sorb sample can be seen visually in fig 2 (c).

The results of our study showed that powders subjected to hot water treatment (aerial parts and roots treated powders of *Ls*) have lower moisture values (fig. 4). Furthermore, the results revealed that those compounds that have an affinity for water were removed from the cellulosic structures of the plant parts subjected to hot water treatment.

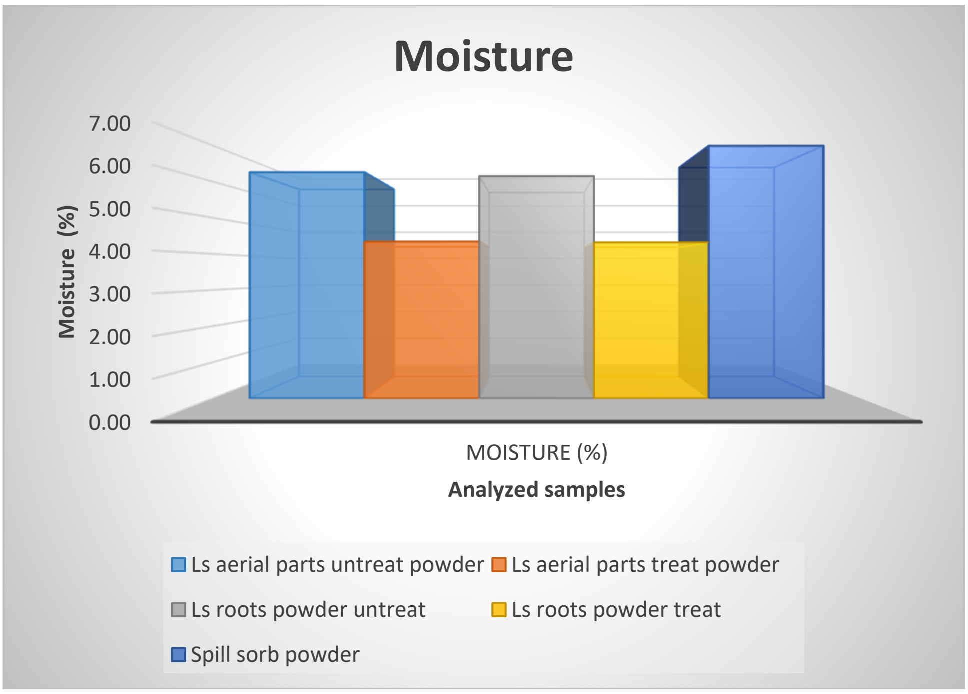

Figure 4. Moisture of tested samples

The visual examination of the results of Fig 2 (c) is also completed by the oil absorption capacity values (Table 1).

Table 1 Comparative results of powder analyzed

Sample	Oil absorption capacity (g/g)
Ls aerial parts untreated powder	26.84±0.5
Ls aerial parts treated powder	25.98±0.3
Ls roots untreated powder	25.10±0.4
Ls roots treated powder	24.54±0.2
Spill Sorb powder	24.24±0.1

These observations are due to the different chemical composition of *Lithrum s.* root, which is known to be rich in lignin and responsible for hydrophobic active groups, compared to the aerial parts of the plant, which are rich in cellulose compounds with active hydrophilic groups [14]. The hot water treatment did only slightly succeed in removing hydrophilic compounds from the aerial parts of the plant. As a consequence, it is necessary that in the future we approach a new strategy with a new method to improve the hydrophobicity of the aerial parts of the *Lythrum salicaria* plant.

4. Future perspectives and Conclusions

Our preliminary study aims to identify a new absorbent, biodegradable, eco-friendly, and low-cost material based on a plant (aerial parts and roots) widely available in nature (*Lythrum salicaria*), with the potential for decontamination, and to improve its hydrophobicity through the use of hot water treatment.

The contaminant used in the test was a petroleum of the REBCO type with a defined density and viscosity.

The study's first goal was to develop and assess the hydrophobicity of powders derived from the aerial and root sections of the *Lithrum salicaria* plant.

The bulk density, moisture content, and absorption capacity of powders derived from the aerial and root sections of the *Lithrum salicaria* plant were determined. The results were compared to those obtained with Spill sorb powder, which is extensively used in the removal of crude-oil products.

Our preliminary research indicates that the *Lithrum salicaria* plant may be a novel natural biosorbent that might be used to clean petroleum products. Additionally, we aim to enhance the hydrophobicity of the plant's aerial parts and to continue testing on seawater and various petroleum compounds in the future (heavy fuel oil, oil, etc).

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