NATURAL WOOL FIBERS: A VIABLE SUBSTITUTE TO COMMERCIALLY AVAILABLE OIL SYNTHETIC SORBENTS

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Romanian Merino wool was tested as a biosorbent for removal of Rebco crude oil from either sea water or distilled water. The wool was packed into two different nets and then placed on the surface of the oily water.

Effects of process parameters, i.e., net mesh density (1.45 and 3.07 mesh/cm^2), concentration of soluble salts in water (0 and 17 g/L), and initial wool mass (10 and 40 g), on the sorption rate and equilibrium wool sorption capacity (2.66-11.89 g/g) were evaluated. Experimental data were processed using kinetic and statistical models.

Keywords: oil spill, sorption capacity, wool fiber, modelling

1. Introduction

Strict ecological legislation, especially in highly developed countries, imposed requirements for the purification of industrial effluents and oil spill cleanup on sea and inland water. Although numerous methods have been developed, the application of sorbents, especially the synthetic ones, is still one of the most efficient techniques to remove the oil spills [1,2].

Recently, natural sorbents based on natural fibers, *e.g*., wool, cotton, kapok, cattail, have attracted attention of scientists [2-9]. These low-cost, renewable, and biodegradable materials can be effective substitutes to commercially available synthetic sorbents that show poor biodegradability [1,2].

Sheep wool is traditionally used in the textile industry for the manufacture of garments, carpets, curtains, covers [10]. Wool fibers possess very good

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mechanical properties and fire resistance, as well as they have different functional groups on their surface, which contribute to the efficient sorption of petroleum products from water [11,12].

Sorption process performances in terms of sorption rate and equilibrium sorption capacity depend on various process factors, *e.g.*, characteristics of sorbent and oily water, contact mode and time, initial sorbent mass.

This paper aimed at studying Romanian Merino wool as a biosorbent for removal of Rebco (Russian export blend) crude oil from either sea water or distilled water. After washing and drying, the wool was packed into a net and placed on the surface of the oily water. The influence of net type, water type, and initial wool mass on sorption kinetics and equilibrium sorption capacity was assessed.

2. Experimental

2.1. Materials

Sheep wool was selected as a sorbent for the removal of petroleum pollutant from the oil-water system. Merino wool was obtained from a local sheep breeder in Romania (Trans-Blan Morosan Comp., Constanta). Raw wool was washed with boiling water and soap, then with distilled water. After that, it was dried at room temperature and further packed into two different nets (N_1 and N_2), which are shown in Fig. 1. Characteristic dimensions and mesh density of both nets are summarized in Table 1.

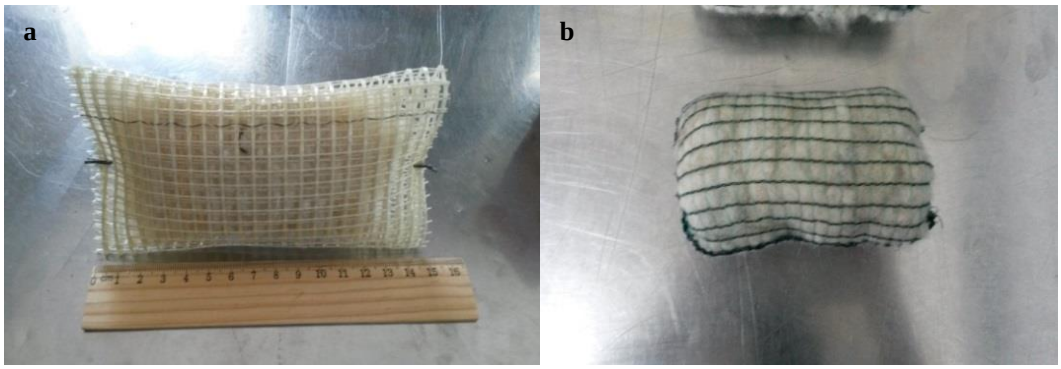

Fig. 1. Nets used as pillow cases: N_1 (a), N_2 (b)

Table 1

Dimensions and mesh density of nets

Type	Length L (cm)	Width l (cm)	Mesh density ρ (mesh/cm^2)
N_1	15	7	3.07
N_2	15	7	1.45

Rebco crude oil, obtained from Oil Terminal Comp., Constanta, Romania, was used as petroleum pollutant. The oil was placed either in sea water (SW) or in distilled water (DW).

2.2. Equipment and procedure

Experimental set-up is shown in Fig. 2. The wool packed into the net was placed on the surface of the oily water from a crystallizer. Rebco crude oil (100 or 400 mL, depending on initial mass of packed bed sorbent, *i.e.*, 10 or 40 g) and 1200 mL of either SW or DW were added in the crystallizer. The system liquid-solid was continuously weighed by an electronic balance (OHAUS AV8101) until the equilibrium state was attained. Wool sorption capacity for Rebco crude oil (q) at time t was calculated using Eq. (1), where m_{oil} is the mass of oil sorbed at time t and m_0 the initial wool mass.

$$q = \frac{m_{oil}}{m_0} \tag{1}$$

Effects of net type (N_1 and N_2), water type (SW and DW), and initial wool mass on the sorption dynamics and equilibrium wool sorption capacity were evaluated.

According to a 2^3-factorial experiment, 8 experimental runs were carried out at room temperature (25 °C). Mesh density of net used as pillow case, ρ (3.07 mesh/cm^2 for N_1 and 1.45 mesh/cm^2 for N_2), concentration of soluble salts in water, c_S (0 g/L for DW and 17 g/L for SW), and initial wool mass, m_0 (10 and 40 g), were selected as quantitative process factors.

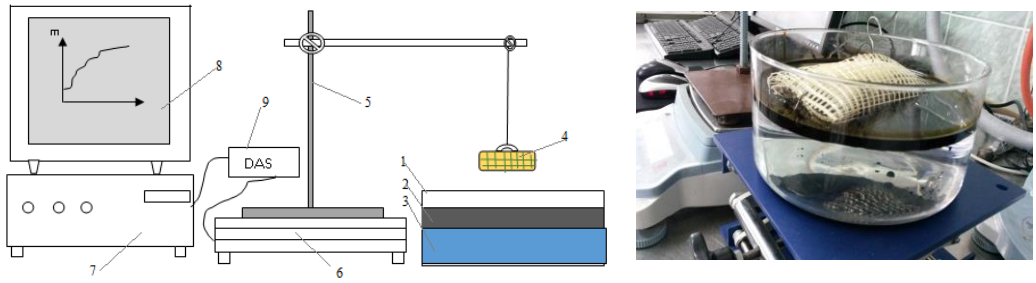

Fig. 2. Experimental set-up: (1) crystallizer, (2) oil layer, (3) water layer, (4) wool fiber sample, (5) system for sample weighing, (6) electronic balance, (7) computer, (8) monitor, (9) data acquisition system

3. Results and discussions

3.1. Experimental data

Experimental dynamics of wool sorption capacity (q) under different operation conditions are shown in Fig. 3. Depicted data emphasize higher values

of q for the net N_2 (with a lower value of mesh density, *i.e.*, ρ=1.45 mesh/cm^2), sea water (SW), and lower value of initial wool mass (m_0=10 g). The equilibrium state was attained after about 5 min for all experimental runs and values of equilibrium wool sorption capacity ($q_{eq,ex}$) in the range of 2.66-11.89 g/g were obtained.

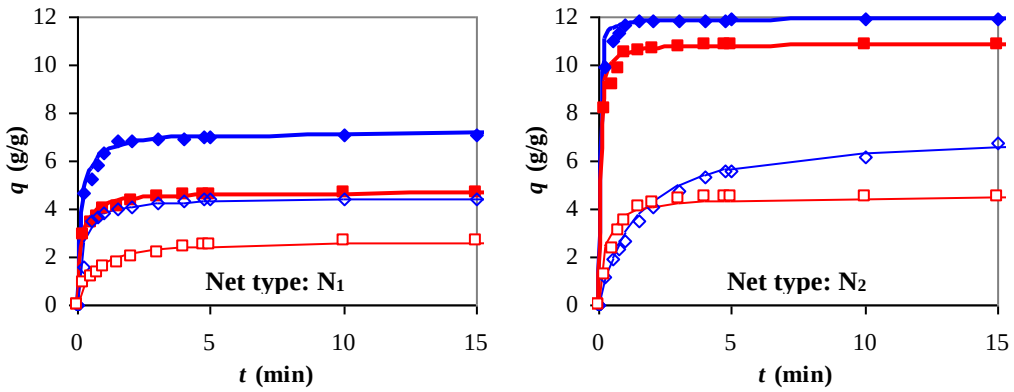

Fig. 3. Effects of process factors on dynamics of wool sorption capacity (q) for Rebco crude oil:
♦ m_0=10 g, SW; ■ m_0=10 g, DW; ◊ m_0=40 g, SW; □ m_0=40 g, DW
(bullets: experimental; lines: Eq. (4))

3.2. Kinetic model

In order to predict the kinetics of sorption process, experimental data were processed using a pseudo-second order rate (PSOR) model given by Eq. (2), where k is the sorption rate constant, q_{eq} the equilibrium sorption capacity, and t the time. PSOR model assumes chemisorption as rate-determining step [4]. Time variation of t/q under different operation conditions is shown in Fig. 4.

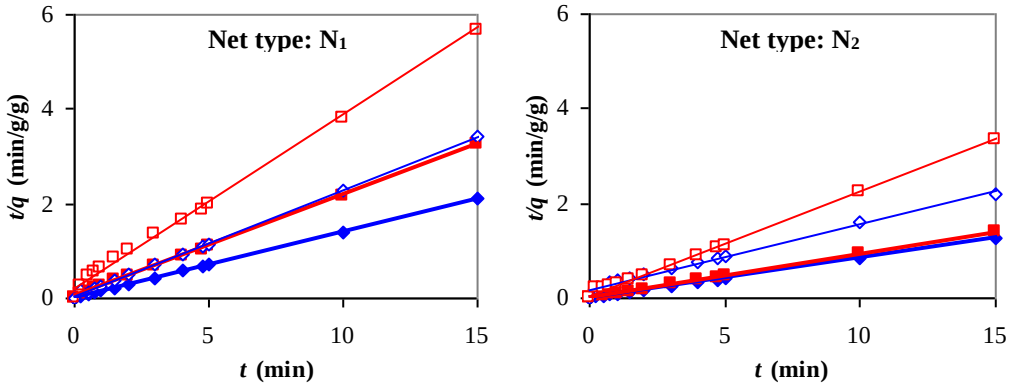

Fig. 4. Characteristic plots of PSOR model:
♦ m_0=10 g, SW; ■ m_0=10 g, DW; ◊ m_0=40 g, SW; □ m_0=40 g, DW

Kinetic parameters k and q_{eq} were regressed from the slope and intercept of the straight lines in Fig. 4. Depicted results reveal that PSOR model determined a very good correlation of experimental data (R^2>0.998). Table 2 contains values of kinetic parameters, those of experimental equilibrium sorption capacity ($q_{eq,ex}$), and percent error (ε) given by Eq. (3). Data listed in Table 2 highlight a good agreement between q_{eq} and $q_{eq,ex}$ ($\varepsilon \leq 5.15\%$).

$$\frac{t}{q} = \frac{t}{q_{eq}} + \frac{1}{k q_{eq}^{\ 2}} \tag{2}$$

Table 2

Kinetic parameters and experimental sorption capacity under different operation conditions

No.	Net type	m_0 (g)	Water type	k (min^{-1})	q_{eq} (g/g)	$q_{eq,ex}$ (g/g)	ε (%)
1	N_1	10	DW	1.56	4.69	4.63	-1.19
2	N_1	10	SW	1.06	7.20	7.20	0.04
3	N_1	40	DW	0.67	2.72	2.66	-2.31
4	N_1	40	SW	1.34	4.47	4.45	-0.48
5	N_2	10	DW	2.21	10.88	10.86	-0.20
6	N_2	10	SW	4.65	11.90	11.89	-0.09
7	N_2	40	DW	1.05	4.53	4.49	-1.01
8	N_2	40	SW	0.10	7.21	6.85	-5.15

$$\varepsilon = 100 \frac{\left(q_{eq,ex} - q_{eq}\right)}{q_{eq,ex}} \tag{3}$$

Values of $q(k,q_{eq},t)$ predicted by Eq. (4), obtained by rearranging the terms in Eq. (2), are shown in Fig. 3 (as lines). A good agreement is observed between experimental and predicted values of sorption capacity (relative standard errors less than 10%).

$$q = \frac{k t q_{eq}^{\ 2}}{1 + k t q_{eq}} \tag{4}$$

3.3. Statistical model

A 2^3 factorial experiment was used to express the kinetic parameters k and q_{eq} depending on process factors. The values of kinetic parameters as well as those of natural factors (ρ, m_0, and c_S) and coded factors (x_1, x_2, and x_3), which were calculated using Eqs. (5)-(7), are summarized in Table 3. Tabulated data were processed according to characteristic procedure of a 2^3 factorial experiment resulting in Eqs. (8) and (9). After eliminating the non-significant terms [13-15], Eq. (9) turned into Eq. (10). Regression equations reveal higher values of kinetic

parameters for lower levels of x_1 (net mesh density) and x_2 (initial wool mass) along with higher values of x_3 (soluble salt concentration in water).

$$x_1 = \frac{\rho - 2.26}{0.81} \tag{5}$$

$$x_2 = \frac{m_0 - 25}{15} \tag{6}$$

$$x_3 = \frac{c_S - 8.50}{8.50} \tag{7}$$

Table 3

Factor levels and response values for 2^3 factorial experiment

No.	Natural factors			Coded factors			Responses	
	ρ (mesh/cm^2)	m_0 (g)	c_S (g/L)	x_1	x_2	x_3	k (min^{-1})	q_{eq} (g/g)
1	3.07	10	0	1	-1	-1	1.56	4.69
2	3.07	10	17	1	-1	1	1.06	7.20
3	3.07	40	0	1	1	-1	0.67	2.72
4	3.07	40	17	1	1	1	1.34	4.47
5	1.45	10	0	-1	-1	-1	2.21	10.88
6	1.45	10	17	-1	-1	1	4.65	11.90
7	1.45	40	0	-1	1	-1	1.05	4.53
8	1.45	40	17	-1	1	1	0.10	7.21

$$k = 1.580 - 0.423\,x_1 - 0.790\,x_2 + 0.207\,x_3 + 0.636\,x_1x_2 - 0.167\,x_1x_3 - \\ - 0.277\,x_2x_3 + 0.571\,x_1x_2x_3 \tag{8}$$

$$q_{eq} = 6.699 - 1.931\,x_1 - 1.967\,x_2 + 0.994\,x_3 + 0.794\,x_1x_2 + \\ + 0.071\,x_1x_3 + 0.112\,x_2x_3 - 0.301\,x_1x_2x_3 \tag{9}$$

$$q_{eq} = 6.699 - 1.931\,x_1 - 1.967\,x_2 + 0.994\,x_3 + 0.794\,x_1x_2 - 0.301\,x_1x_2x_3 \tag{10}$$

4. Conclusions

Ability of Romanian Merino wool to retain Rebco crude oil from sea water (SW) or distilled water (DW) was studied. Sorption tests were performed under various experimental conditions. Raw wool was washed with boiled water and soap, then with DW, further was dried, packed into two different nets, and further placed on the surface of the oily water.

The influence of net type (quantified as mesh density, ρ (1.45 and 3.07 mesh/cm^2)), water type (quantified as concentration of soluble salts in water, c_S (0

g/L for DW and 17 g/L for SW)), and initial wool mass, m_0 (10 and 40 g) on the sorption rate and equilibrium wool sorption capacity (2.66-11.89 g/g) was evaluated. The equilibrium was attained after about 5 min for all tests conducted. Sorption process was faster, and values of equilibrium sorption capacity were higher for the net with a lower value of mesh density (ρ=1.45 mesh/cm^2), SW, and lower value of initial wool mass (m_0=10 g).

Wool sorption capacity was predicted by processing the experimental data using a pseudo-second order rate model. By applying this model, assuming chemisorption as rate-determining step, a very good correlation of experimental data (R^2>0.998) was obtained. Moreover, a good agreement between experimental and predicted values of equilibrium wool sorption capacity (percent errors less than 5.15%) was noticed. Regression equations based on a 2^3 factorial plan were established among the model kinetic parameters (sorption rate constant and equilibrium sorption capacity) and dimensionless process factors.

The results of this study highlight that Romanian Merino wool without any chemical pretreatment could be successfully used as a natural sorbent for the removal of oil from the water-oil system.

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