Natural Wool for Removal of Oil Spills from Water Surface

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Romanian Merino wool was tested as a natural sorbent for oil spill cleanup. Rebco crude oil placed in distilled water was used as an oily water model. Experiments of batch sorption were performed under various conditions. The effects of process factors, i.e., initial density of packed bed sorbent (0.05-0.99 g/cm^3), initial volume ratio of oil and water (0.25 and 0.14 cm^3/cm^3), and contact surface between adsorbent and oily water, on wool sorption capacity (6.4-11.8 g/g) were evaluated. Experimental data were fitted using pseudo-first order rate and pseudo-second order rate models.

Keywords: oil spill, kinetic model, sorption capacity, wool fibre

Exploration, production, transport, and storage of oil involve the risk of its spillage that can have harmful effects on the environment and human health [1-6]. Usually, the oil spilled in the water is burned, dispersed or removed by mechanical skimmers or sorbents [2,3,5,7].

Sorption is an effective technique which is widely applied for water remediation and pollutant recovery [1-17]. Synthetic organic materials, *e.g.*, acrylic resins, polyurethane foams, polypropylene and polyester fibres, are the most used sorbents for oil removal and recovery [2,4,5,11]. They possess good oleophilic and hydrophobic properties, but are non-biodegradable and generally expensive [1-5,11]. Renewable, biodegradable, and cheap natural sorbents, including wool, coconut coir, cotton, kapok, silk-floss, sisal leaves, palm leaves, sponge gourd, cattail, milkweed, activated carbon, sawdust, rice husk, coconut husk, walnut shell, bagasse, wood chips, human hair, have been extensively tested lately for oil spill removal [1-7,9-17]. Oil sorption using wool and wool-based sorbents can be an attractive method for water remediation due to their low cost, availability, biodegradability, buoyancy, hydrophobicity, and high sorption capacity [3,6,9,12-17].

Sorption capacity and process kinetics mainly depend on oil and sorbent type, initial volume ratio of oil and water, sorbent dosage, contact time, contact surface between sorbent and oily water, temperature and *p*H of oily water.

This paper aimed at testing Romanian Merino wool as a natural sorbent for oil spill cleanup. Rebco crude oil placed in distilled water was used as an oily water model. The effects of process factors in terms of initial density of packed bed sorbent, initial volume ratio of oil and water, and contact surface between adsorbent and oily water were evaluated.

Experimental part

Materials

Romanian Merino wool provided by TRANS-BLAN MOROSAN (Romania) was used as organic sorbent and Rebco crude oil placed in distilled water as oily water. Crude oil was analyzed in the Laboratory of Oil Terminal Constanta (Romania) and its main physical characteristics are given in table 1.

Table 1

PHYSICAL PROPERTIES OF REBCO CRUDE OIL AT 22 °C

Density (g/cm^3)	0.86
Kinematic viscosity (cSt)	7.84
Dynamic viscosity (cP)	6.74
Surface tension (dyn/cm)	30.1

Procedure

The sorbent was packed into a support and placed in the oily water sample. The system was further shaken in a laboratory shaker (600 rpm) and the sorbent was weighed from 5 to 5 min, until the equilibrium was attained. Wool sorption capacity for the crude oil, q (g/g), was determined by eq. (1), where m_0 (g) is the initial sorbent mass and m (g) the wet sorbent mass (after draining).

$$q = \frac{m - m_0}{m_0} \quad (1)$$

Two experimental runs of batch sorption were performed, according to the support type (fig. 1). A cylindrical support (46 mm diameter, 60 mm height) with 35 holes (2 mm diameter) at the bottom (fig. 1a) was used in experimental run 1 and a flat support (62 mm diameter, 4 mm height) with 101 holes of 2 mm diameter (fig. 1b) in the experimental run 2.

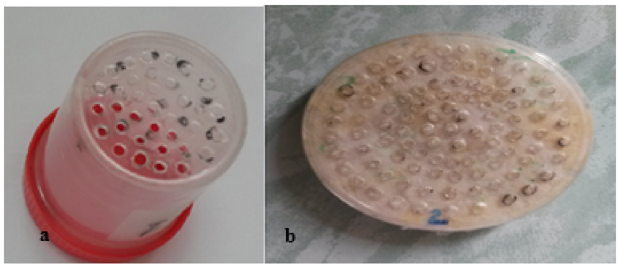

Fig 1. Supports used in the experimental runs 1 (a) and 2 (b).

Experimental run 1

The sorbent packed into the cylindrical support (fig. 1a) was placed in a flask containing the oily water sample (150 cm^3 of Rebco crude oil in 600 cm^3 distilled water) and the system was shaken until the equilibrium was attained. Two experiments corresponding to values of initial wool mass (m_0) of 5 and 10 g were performed at room temperature (22 °C).

Experimental run 2

The sorbent packed into the flat support (fig. 1b) was placed in a crystallizer containing the oily water sample (250 cm^3 of Rebco crude oil in 1800 cm^3 distilled water)

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and the system was shaken until the equilibrium was attained. Three experiments corresponding to values of initial wool mass (m_0) of 4, 8, and 12 g were performed at room temperature (22 °C).

Modelling

Modelling is an effective tool for describing, designing, and optimizing unit operations and chemical processes [18-21]. Pseudo-first and pseudo-second order rate equations have been widely applied to describe batch sorption kinetics [5, 17, 22-30].

Pseudo-first order rate (PFOR) expression of Lagergren [26] is given by eq. (2), where q and q_{eq} are the sorption capacities at time τ and at equilibrium, respectively, and k_1 is the rate constant of PFOR. Eqs. (3)-(5) were obtained from Eq. (2) by separating the variables, integrating, and rearranging the terms. According to eq. (4), kinetic parameters k_1 and q_{eq} can be obtained from the slope and intercept of the straight line given by a plot of ln(q_{eq}-q) *vs.* τ.

$$\frac{dq}{d\tau} = k_1\left(q_{eq} - q\right) \tag{2}$$

$$\int_0^q \frac{1}{q_{eq} - q} dq = \int_0^\tau k_1 d\tau \tag{3}$$

$$\ln\left(q_{eq} - q\right) = \ln q_{eq} - k_1\tau \tag{4}$$

$$q = q_{eq}\left(1 - e^{-k_1\tau}\right) \tag{5}$$

Pseudo-second order rate (PSOR) is expressed by eq. (6), where q and q_{eq} are the sorption capacities at time τ and at equilibrium, respectively, and k_2 is the rate constant of PSOR. Eqs. (7)-(10) resulted from eq. (6) by separating the variables, integrating, and rearranging the terms. According to eq. (10), kinetic parameters q_{eq} and k_2 can be estimated from the slope and intercept of the straight line given by a plot of τ/q *vs.* τ.

$$\frac{dq}{d\tau} = k_2\left(q_{eq} - q\right)^2 \tag{6}$$

$$\int_0^q \frac{1}{\left(q_{eq} - q\right)^2} dq = \int_0^\tau k_2 d\tau \tag{7}$$

$$\frac{1}{q_{eq} - q} = \frac{1}{q_{eq}} + k_2\tau \tag{8}$$

$$q = \frac{k_2 \tau q_{eq}^2}{1 + k_2 \tau q_{eq}} \tag{9}$$

$$\frac{\tau}{q} = \frac{\tau}{q_{eq}} + \frac{1}{k_2 q_{eq}^2} \tag{10}$$

Results and discussions

Experimental data

Experimental run 1

The effects of initial density of packed bed wool, ρ_{b0} (0.05 and 0.10 g/cm^3), on the dynamics of wool sorption capacity for Rebco crude oil are highlighted in fig. 2. Depicted results reveal that for an initial volume ratio of oil and water (R_0) of 0.25 cm^3/cm^3, the equilibrium was attained at τ_{eq}=35 min and equilibrium sorption capacity ($q_{eq,exp}$) was 7.092 g/g for ρ_{b0}=0.05 g/cm^3 and 6.381 g/g for ρ_{b0}=0.10 g/cm^3. Moreover, the values of initial oil sorption rate, calculated for the first 5 min, were almost equal, *i.e.*, r_0≈0.93 g/g/min, for both values of ρ_{b0}, whereas those of sorption rate (r=dq/dτ) for τ>5 min were slightly lower for ρ_{b0}=0.10 g/cm^3. Accordingly, for a double value of initial density of packed bed sorbent (ρ_{b0}=0.10 g/cm^3), values of $q_{eq,exp}$ were 1.11 times lower, those of r=dq/dτ (τ>5 min) were lower, and τ_{eq} and r_0 were similar. In this experimental run, about half of the cylindrical support containing the wool was immersed in the oily water (fig. 3).

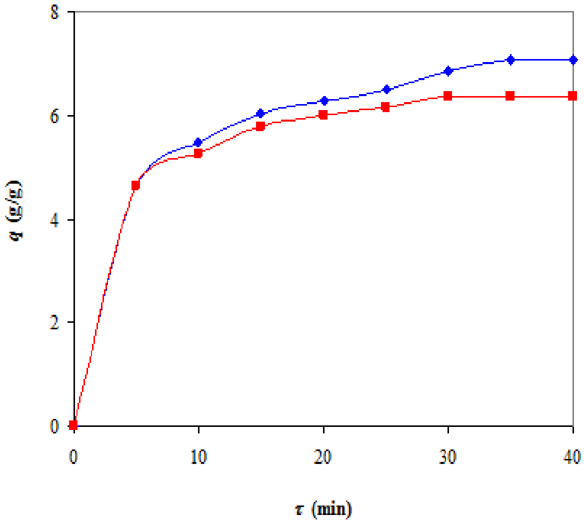

Fig. 2. Experimental dynamics of wool sorption capacity (q) for Rebco crude oil depending on initial density of packed bed wool (ρ_{b0}) for experimental run 1: ♦ρ_{b0}=0.05 g/cm^3, ■ρ_{b0}=0.10 g/cm^3 (initial volume ratio of oil and water: R_0=0.25 cm^3/cm^3)

Fig. 3. Crude oil retained by the wool packed into the cylindrical support (ρ_{b0}=0.05 g/cm^3) after 20 min

Experimental run 2

Data given in fig. 4, highlighting the effects of initial density of thin-bed wool, ρ_{b0} (0.33, 0.66, and 0.99 g/cm^3), on the dynamics of wool sorption capacity for Rebco crude oil (corresponding to flat support and R_0=0.14 cm^3/cm^3), emphasize the following issues: (i) τ_{eq}=35 min and $q_{eq,exp}$=11.76 g/g for ρ_{b0}=0.33 g/cm^3, τ_{eq}=25 min and $q_{eq,exp}$=8.094 g/g for ρ_{b0}=0.66 g/cm^3, τ_{eq}=25 min and $q_{eq,exp}$=10.88 g/g for ρ_{b0}=0.99 g/cm^3; (ii) r_0=1.20 g/g/min for ρ_{b0}=0.33 g/cm^3, r_0=0.60 g/g/min for ρ_{b0}=0.66 g/cm^3, r_0=1.01 g/g/min for ρ_{b0}=0.99 g/cm^3. For each experiment in this experimental run, the flat support containing the wool floated on the surface of oily water (fig. 5).

Predicted data

Characteristic plots of PFOR and PSOR models, *i.e.*, ln(q_{eq}-q) *vs.* τ and τ/q *vs.* τ, for experimental runs 1 and 2 are shown in figs. 6 and 7. Kinetic parameters k_1, k_2, and q_{eq}, obtained from the slope and intercept of the straight lines in figs. 6 and 7, as well as their corresponding

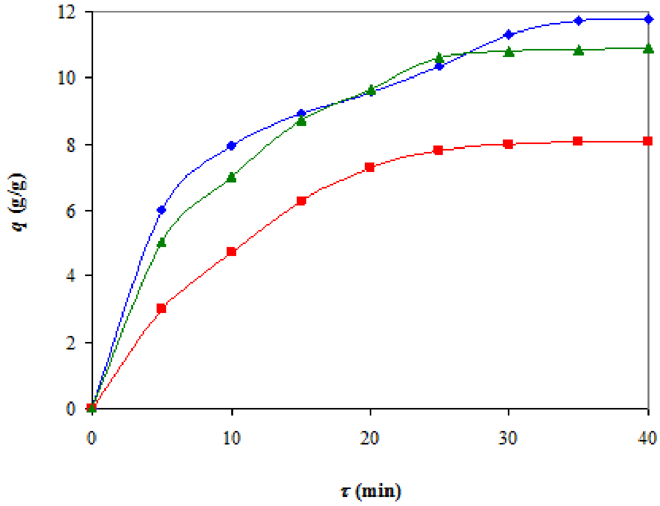

Fig. 4. Experimental dynamics of wool sorption capacity (q) for Rebco crude oil depending on initial density of thin-bed wool (ρ_{b0}) for experimental run 2: ♦ ρ_{b0}=0.33 g/cm^3, ■ ρ_{b0}=0.66 g/cm^3, ▲ ρ_{bo}=0.99 g/cm^3 (initial volume ratio of oil and water: R_0=0.14 cm^3/cm^3).

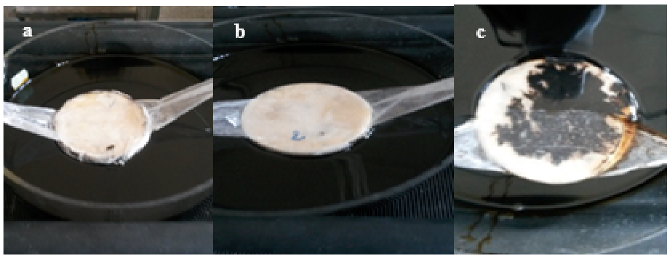

Fig. 5. Thin-bed wool floating on the surface of oily water after 10 min: (a) ρ_{b0}=0.33 g/cm^3, (b) ρ_{b0}=0.66 g/cm^3, (c) ρ_{b0}=0.99 g/cm^3.

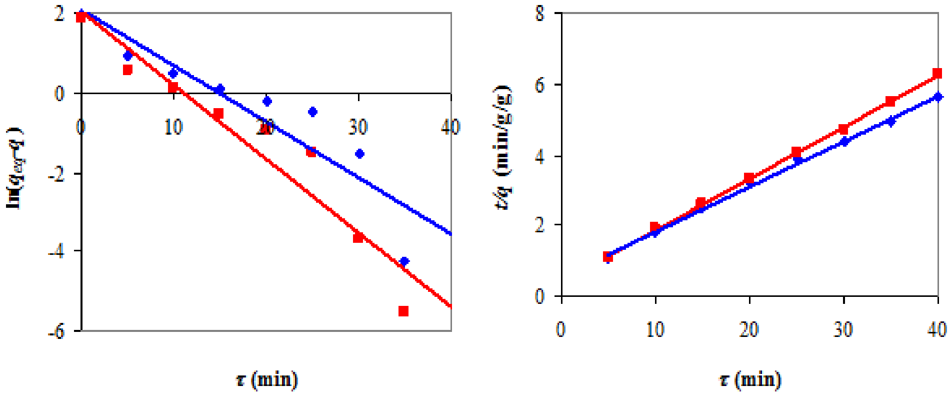

Fig. 6. Characteristic plots of PFOR (a) and PSOR (b) models for experimental run 1: ♦ ρ_{b0}=0.05 g/cm^3, ■ ρ_{b0}=0.10 g/cm^3 (R_0=0.25 cm^3/cm^3).

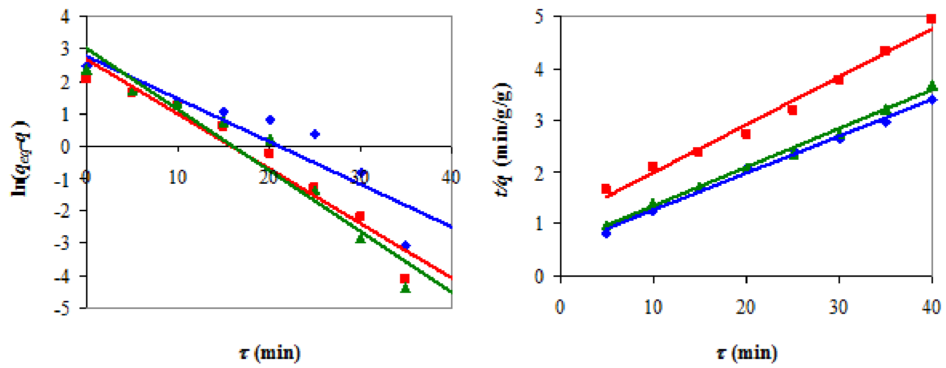

Fig. 7. Characteristic plots of PFOR (a) and PSOR (b) models for experimental run 2: ♦ ρ_{b0}=0.33 g/cm^3, ■ ρ_{b0}=0.66 g/cm^3, ▲ ρ_{b0}=0.99 g/cm^3 (R_0=0.14 cm^3/cm^3).

Table 2
KINETIC PARAMETERS OF PFOR AND PSOR MODELS FOR EXPERIMENTAL RUN 1

R_0 (cm^3/cm^3)	ρ_{b0} (g/cm^3)	$q_{eq,exp}$ (g/g)	PFOR model				PSOR model			
			q_{eq} (g/g)	k_1 (min^{-1})	RSD (%)	R^2	q_{eq} (g/g)	k_2 (min^{-1})	RSD (%)	R^2
0.25	0.05	7.092	7.915	0.140	192.5	0.8425	7.805	0.030	2.17	0.9978
	0.10	6.381	7.778	0.186	57.47	0.9157	6.845	0.054	1.04	0.9995

Table 3
KINETIC PARAMETERS OF PFOR AND PSOR MODELS FOR EXPERIMENTAL RUN 2

R_0 (cm^3/cm^3)	ρ_{b0} (g/cm^3)	$q_{eq,exp}$ (g/g)	PFOR model				PSOR model			
			q_{eq} (g/g)	k_1 (min^{-1})	RSD (%)	R^2	q_{eq} (g/g)	k_2 (min^{-1})	RSD (%)	R^2
0.14	0.33	11.76	15.96	0.131	141.6	0.8485	14.07	0.009	3.24	0.9935
	0.66	8.094	14.44	0.169	177.2	0.9440	10.89	0.008	4.49	0.9845
	0.99	10.88	20.76	0.188	237.8	0.9338	13.45	0.009	2.95	0.9946

determination coefficients (R^2) and relative standard deviations (RSD) are presented in tables 2 and 3. Tabulated data highlight that PSOR model, considering chemisorption as rate-determining step [22-24,27,29], provides a better correlation of experimental data ($0.9845 \le R^2 \le 0.9995$, $1.04\% \le RSD \le 4.49\%$) than PFOR model ($0.8425 \le R^2 \le 0.9440$, $57.47\% \le RSD$d"237.8%). Moreover, the values of q_{eq} corresponding to PSOR model are closer to those determined experimentally ($q_{eq,exp}$). Values of q calculated using eqs. (5) and (9) are presented in figs. 8 and 9. Depicted data emphasize a good agreement between experimental and predicted results ($RSD \le 2.87\%$ for experimental run 1 and $RSD \le 4.34\%$ for experimental run 2).

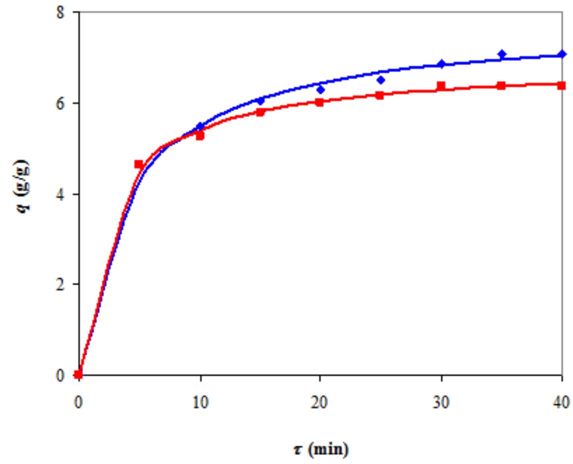

Fig. 8. Experimental and predicted (eq. (5)) dynamics of wool sorption capacity (q) for Rebco crude oil depending on initial density of packed bed wool (ρ_{b0}) for experimental run 1: ♦ ρ_{b0}=0.05 g/cm^3, ■ ρ_{b0}=0.10 g/cm^3 (initial volume ratio of oil and water: R_0=0.25 cm^3/cm^3).

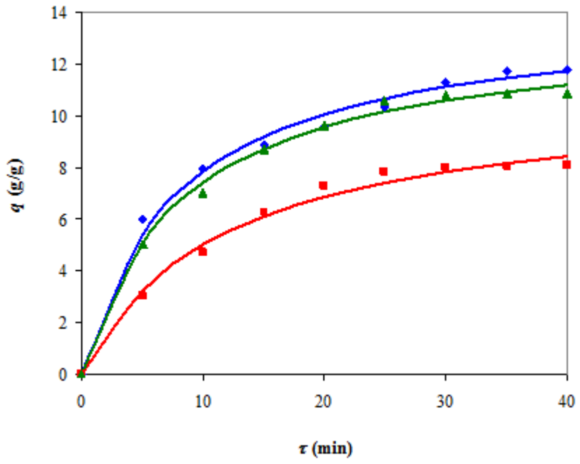

Fig. 9. Experimental and predicted (eq. (9)) dynamics of wool sorption capacity (q) for Rebco crude oil depending on initial density of thin-bed wool (ρ_{b0}) for experimental run 2: ♦ ρ_{b0}=0.33 g/cm^3, ■ ρ_{b0}=0.66 g/cm^3, ▲ ρ_{b0}=0.99 g/cm^3 (initial volume ratio of oil and water: R_0=0.14 cm^3/cm^3)

Conclusions

The capacity of natural wool to retain crude oil from water was investigated. Experiments of batch sorption were conducted under different conditions. The wool was packed into a cylindrical or a flat support, placed in a mixture of Rebco crude oil and water, and further the system was shaken in a laboratory shaker.

The effects of initial density of packed bed wool (ρ_{b0}), initial volume ratio of oil and water (R_0), and support type on the sorption capacity (q) were evaluated. For the cylindrical support, an equilibrium state was attained after 35 min (for R_0=0.25 cm^3/cm^3) and equilibrium values of q were 7.092 g/g for ρ_{b0}=0.05 g/cm^3 and 6.381 g/g for ρ_{b0}=0.10 g/cm^3. For the flat support, equilibrium state was attained after 25-35 min (for R_0=0.14 cm^3/cm^3) and equilibrium values of q were 11.76 g/g for ρ_{b0}=0.33 g/cm^3, 8.094 g/g for ρ_{b0}=0.66 g/cm^3, and 10.88 g/g for ρ_{b0}=0.99 g/cm^3. Equilibrium values of q determined for both support types are consistent with those reported in the related literature for oil sorption using wool-based sorbents [6,9,13-16]. Experimental data were correlated using pseudo-first order rate (PFOR) and pseudo-second order rate (PSOR) models. PSOR model, assuming chemisorption as rate-determining step, provided a better correlation of experimental results.

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