Romanian Merino Wool Sorbent for Oil Spill Cleanup

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Removal of some pollutants (Basra, Azeri, and Rebco crude oils, diesel, gasoline, and 1/1 (w/w) diesel-gasoline mixture) from water by sorption using Romanian Merino wool as a natural sorbent was studied in this paper. Batch experiments were conducted at different levels of initial sorbent mass (1 and 3 g), oily water pH (5 and 10), and operating temperature (30 and 45 °C). The effects of these factors on wool sorption capacity were evaluated. The sorption capacity of more viscous fuels (crude oils), i.e., 4.13-21.87 g/g, increased with an increase in oily water pH and a decrease in initial sorbent mass and temperature. For less viscous pollutants (diesel, gasoline, and their mixture), the sorption capacity (3.32-9.19 g/g) increased with a decrease in sorbent mass, the effects of pH and temperature being negligible. Experimental results were processed according to a 2^3 factorial plan and regression equations between the process factors and sorption capacity were obtained. SEM analysis revealed that the removal process was governed by both adsorption and absorption mechanisms.

Keywords: oil spill, sorption capacity, wool fibre, factorial experiment

Remediation of oil spills in open waters is a research topic of great importance. As suitable sorbents are selected, sorption is a simple, feasible, and effective option for oil removal from water [1, 2].

Synthetic polymers including polyurethane foams, acrylic resins, polypropylene and polyester fibres are widely used sorbents at present [3]. Natural organic sorbents based on various fibres, *e.g.*, wool, cotton, cattail, sisal, coir, sponge gourd, silk floss, kapok, milkweed, are attractive alternative to synthetic ones [1-11]. Due to their high sorption capacity, buoyancy, hydrophobicity, reusability, biodegradability, and availability, wool and wool-based products can be very effective sorbents to clean up the oil spills [7-10].

Oily water treatment using fibrous sorbents generally involves both adsorption onto the fibre surface and absorption inside the fibre [1-4,8,11]. Process performances, commonly expressed in terms of oil removal efficiency (%) and sorbent sorption capacity (g oil/g sorbent), depend on various process factors including sorbent and oil characteristics, sorbent dosage, initial oil concentration, contact time, oily water pH and temperature [1-11].

This paper aimed at studying a simple batch sorption procedure for oily water treatment using Romanian Merino wool as a natural sorbent. Fuel (Basra, Azeri, and Rebco crude oils, diesel, gasoline, and diesel-gasoline mixture) placed in demineralised water was used as an oily water model. The effects of process factors in terms of initial sorbent mass, oily water *p*H, and operating temperature on the wool sorption capacity were evaluated based on a 2^3 experimental plan.

Experimental part

Materials and methods

Organic sorbent was Romanian Merino wool provided by TRANS-BLAN MOROSAN (Romania). Fuel (Basra, Azeri, and Rebco crude oils, diesel, gasoline, and 1/1 (w/w) diesel-gasoline mixture) placed in demineralised water was used as oily water. The pollutants were characterized in the Laboratory of Oil Terminal Constanta (Romania) and their main physical characteristics are presented in table 1.

The sorbent was placed in a 500 mL flask containing the oily water sample (10 g of fuel in 300 mL demineralised water). The flask was shaken in a laboratory shaker (600 rpm) for 30 min. The wet sorbent was then removed, let to drain for 1 min, and further weighed.

Wool fibre morphology was analyzed using a HITACHI S2600M scanning electron microscope.

Process variables

Batch experiments were performed for each oily water sample at 2 levels of process factors, *i.e.*, initial sorbent mass (m=1, 3 g), oily water *p*H (pH=5, 10), and operating temperature (t=30, 45 °C). Wool sorption capacity, q (g/g), was determined by eq. (1), where m_f (g) is the mass of wet sorbent after draining.

$$q = \frac{m_f - m}{m} \tag{1}$$

Results and discussions

Wool sorption capacity

The effects of process factors (m=1, 3 g, pH=5, 10, and t=30, 45 °C) on sorption capacities of wool sorbent for i fuel (q_i, i=1..6) solutions are highlighted in table 2 and figure 1. The values of q_i under the experimental conditions considered in this study were as follows: q_1=4.13-20.70 g/g for Basra crude oil, q_2=4.45-15.84 g/g for Azeri crude oil, q_3=4.97-21.87 g/g for Rebco crude oil, q_4=4.47-9.19 g/g for diesel fuel, q_5=3.32-8.17 g/g for gasoline, and q_6=3.55-8.74 g/g for 1/1 (w/w) diesel-gasoline mixture.

Table 1
PHYSICAL PROPERTIES OF POLLUTANTS

Parameter	Temperature (°C)	Basra crude oil	Azeri crude oil	Rebco crude oil	Diesel	Gasoline	Diesel-gasoline mixture
Density (g/cm^3)	15	0.91	0.85	0.87	0.83	0.75	0.79
Viscosity (cSt)	20	8.64	6.9	7.84	5.1	0.5	2.6

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Table 2
WOOL SORPTION CAPACITY DEPENDING ON PROCESS FACTORS

i	Fuel	Exp.	m (g)	pH	t (°C)	q_i (g/g)	i	Fuel	Exp.	m (g)	pH	t (°C)	q_i (g/g)
1	Basra crude oil	1	1	5	30	13.35	4	Diesel	25	1	5	30	8.77
		2	3	5	30	7.99			26	3	5	30	4.47
		3	1	10	30	20.70			27	1	10	30	9.12
		4	3	10	30	8.09			28	3	10	30	6.59
		5	1	5	45	11.22			29	1	5	45	9.02
		6	3	5	45	4.13			30	3	5	45	4.47
		7	1	10	45	12.79			31	1	10	45	9.19
		8	3	10	45	7.09			32	3	10	45	5.25
2	Azeri crude oil	9	1	5	30	9.23	5	Gasoline	33	1	5	30	7.11
		10	3	5	30	7.05			34	3	5	30	3.34
		11	1	10	30	15.84			35	1	10	30	8.17
		12	3	10	30	9.48			36	3	10	30	4.25
		13	1	5	45	9.13			37	1	5	45	7.50
		14	3	5	45	4.45			38	3	5	45	3.32
		15	1	10	45	12.86			39	1	10	45	7.66
		16	3	10	45	5.80			40	3	10	45	4.70
3	Rebco crude oil	17	1	5	30	13.99	6	Diesel-gasoline mixture	41	1	5	30	7.51
		18	3	5	30	6.94			42	3	5	30	3.55
		19	1	10	30	21.87			43	1	10	30	7.73
		20	3	10	30	9.48			44	3	10	30	4.88
		21	1	5	45	9.78			45	1	5	45	8.70
		22	3	5	45	4.97			46	3	5	45	4.03
		23	1	10	45	9.90			47	1	10	45	8.74
		24	3	10	45	6.37			48	3	10	45	5.62

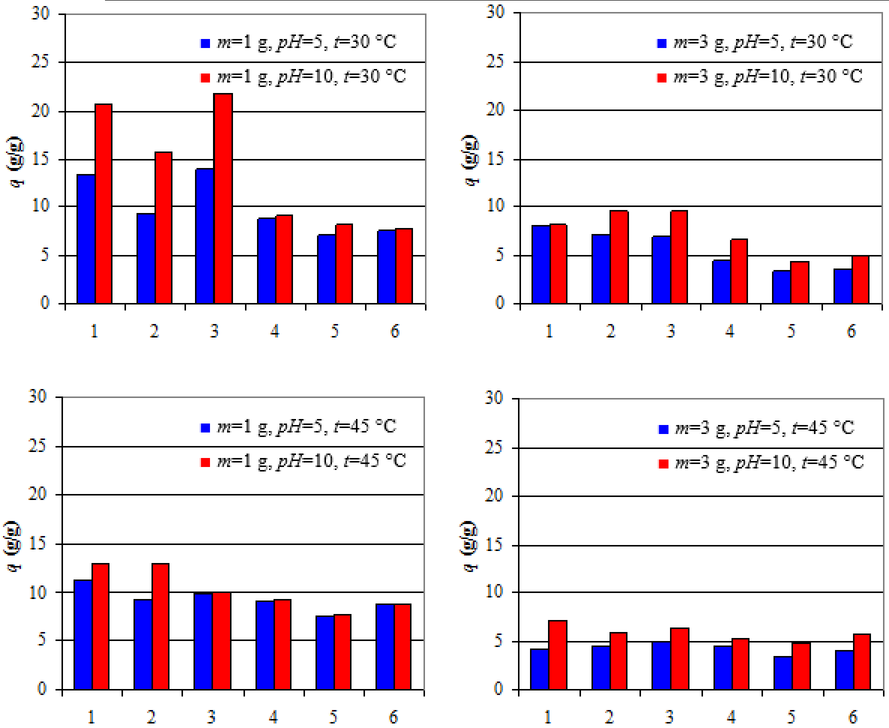

Fig. 1. The effect of process factors on wool sorption capacity: (1) Basra crude oil, (2) Azeri crude oil, (3) Rebco crude oil, (4) diesel, (5) gasoline, (6) 1/1 (w/w) diesel-gasoline mixture

Tabulated and depicted results indicate a decrease in sorption capacities (up to 2.7 and 1.7 times, respectively) with an increase in initial sorbent mass and a decrease in solution pH for all fuel solutions. Moreover, for more viscous fuels (i=1..3) the sorption capacity decreased (up to 2.2 times) with an increase in operating temperature, whereas the effect of temperature was almost negligible for less viscous ones (i=4..6). For the low level of operating temperature (t=30 °C), q_i values of more viscous fuels (6.94-21.87 g/g) are up to 2.8 times larger than those of less viscous pollutants (3.34-9.12 g/g).

Experimental data were processed according to characteristic procedure of a 2^3 factorial experiment [12-14]. Dimensionless factors are given by eqs. (2)-(4), were m_c=2 g, pH_c=7.5, and t_c=37.5 °C are center-points. The effects of dimensionless process factors on wool sorption capacity are expressed by eqs. (5)-(10).

$$x_1 = \frac{m-2}{1} \tag{2}$$

$$x_2 = \frac{pH-7.5}{2.5} \tag{3}$$

$$x_3 = \frac{t-37.5}{7.5} \tag{4}$$

$$q_1 = 10.670 - 3.845x_1 + 1.497x_2 - 1.862x_3 - 0.732x_1x_2 + 0.647x_1x_3 - 0.365x_2x_3 + 1.080x_1x_2x_3 \quad (5)$$

$$q_2 = 9.230 - 2.535x_1 + 1.765x_2 - 1.170x_3 - 0.820x_1x_2 - 0.400x_1x_3 - 0.495x_2x_3 + 0.225x_1x_2x_3 \quad (6)$$

$$q_3 = 10.413 - 3.472x_1 + 1.493x_2 - 2.658x_3 - 0.507x_1x_2 + 1.388x_1x_3 - 1.113x_2x_3 + 0.827x_1x_2x_3 \quad (7)$$

$$q_4 = 7.110 - 1.915x_1 + 0.428x_2 - 0.128x_3 + 0.297x_1x_2 - 0.208x_1x_3 - 0.190x_2x_3 - 0.145x_1x_2x_3 \quad (8)$$

$$q_5 = 5.756 - 1.854x_1 + 0.439x_2 + 0.039x_3 + 0.134x_1x_2 + 0.069x_1x_3 - 0.054x_2x_3 + 0.171x_1x_2x_3 \quad (9)$$

$$q_6 = 6.345 - 1.825x_1 + 0.398x_2 + 0.428x_3 + 0.332x_1x_2 - 0.122x_1x_3 + 0.010x_2x_3 + 0.055x_1x_2x_3 \quad (10)$$

Eqs. (11)-(16), obtained by eliminating the non-significant terms in eqs. (5)-(10) [12-15], indicate the following issues: (i) the values of wool sorption capacity corresponding to crude oils (q_1, q_2, and q_3) are higher for a higher pH (x_2) as well as lower levels of initial sorbent mass (x_1) and operating temperature (x_3); (ii) for diesel, gasoline, and diesel-gasoline mixture, the values of q_4, q_5, and q_6 are higher for a lower level of initial sorbent mass (x_1) and the effects of pH (x_2) and operating temperature (x_3) can be neglected.

$$q_1 = 10.670 - 3.845x_1 + 1.497x_2 - 1.862x_3 \quad (11)$$

$$q_2 = 9.230 - 2.535x_1 + 1.765x_2 - 1.170x_3 \quad (12)$$

$$q_3 = 10.413 - 3.472x_1 + 1.493x_2 - 2.658x_3 + 1.388x_1x_3 \quad (13)$$

$$q_4 = 7.110 - 1.915x_1 \quad (14)$$

$$q_5 = 5.756 - 1.854x_1 \quad (15)$$

$$q_6 = 6.345 - 1.825x_1 \quad (16)$$

SEM analysis

SEM images of wool sorbent before sorption (fig. 2) highlight 20-60 μm diameter fibres covered by flat scales arranged compactly. SEM analysis results of wool fibres after 3 min of sorption (fig. 3) indicate that the process was governed by both adsorption and absorption mechanisms.

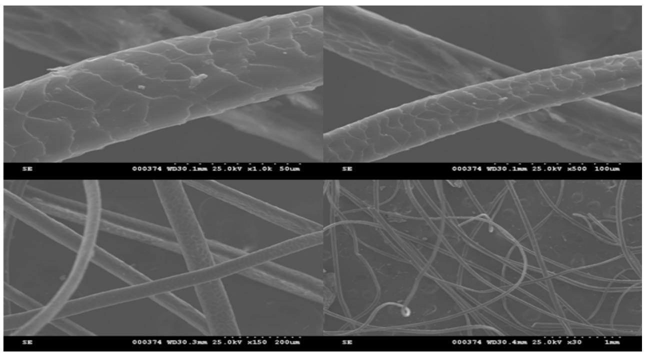

Fig. 2. SEM images of wool fibres before sorption

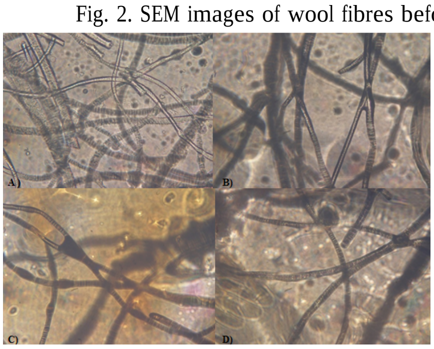

Fig. 3. SEM images of wool fibres after 3 min of sorption: (A) 1/1 (w/w) diesel-gasoline mixture, (B) gasoline, (C) Basra crude oil, (D) Azeri crude oil

Conclusions

Batch sorption tests for oily water treatment using Romanian Merino wool as a natural sorbent were conducted under different experimental conditions. Fuel pollutant (Basra, Azeri, and Rebco crude oils, diesel, gasoline, and 1/1 (w/w) diesel-gasoline mixture) placed in demineralised water was used as an oily water model. Initial sorbent mass (m=1, 3 g), oily water pH (pH=5, 10), and operating temperature (t=30, 45 °C) were selected as process factors. The effects of these factors on wool sorption capacity (q=3.32-21.87 g/g) were evaluated. Experimental results emphasized the following issues: (i) a decrease in q (up to 2.7 and 1.7 times, respectively) with an increase in m and a decrease in pH for all fuel solutions; (ii) for more viscous fuels (crude oils), q (4.13-21.87 g/g) decreased (up to 2.2 times) with an increase in t, whereas for less viscous ones (diesel, gasoline, and their mixture), the effect of t on q (3.32-9.19 g/g) was almost negligible; (iii) for t=30 °C, q values of more viscous fuels (6.94-21.87 g/g) are up to 2.8 times larger than those of less viscous ones (3.34-9.12 g/g). Experimental data were processed based on a 2^3 factorial plan and regression equations between the process factors and wool sorption capacity were determined. SEM analysis indicated that the removal process was governed by both adsorption and absorption mechanisms.

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Manuscript received: 21.02.2018