Use of Assaf Sheep Wool for Bioretention of Hydrocarbons (diesel) in Water Bodies

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Assaf sheep wool is not used as a textile fiber because of its high keratin content and thickness. This sheep is only used for its milk and meat production, and its wool can be used as a biosorbent for the removal of hydrocarbons. Thus, this research studied the effect of the use of Assaf sheep wool for the bioretention of hydrocarbons present in water bodies. For the experimental development, the wool was characterized and synthetic water composed of a mixture of 6 L of hydrocarbon (petroleum) and 20 L of water was used. The treatment was carried out with different doses of wool (40, 60, 80, 100, 120, 140 and 160 g) arranged in pads of 15 cm x 10 cm, and worked as a function of pH and contact time. The wool characterization results showed a diameter of 34 μm, which is considered thick and not useful for textile production. On the other hand, the maximum bioretention (94.10 %) of hydrocarbons was achieved with a dosage of 120 g and a contact time of 150 s. Finally, it is concluded that Assaf sheep wool is a good absorbent for bioretention of hydrocarbons (petroleum), and could be applied in water sources contaminated with these compounds.

1. Introduction

Worldwide, 98,000,000.85 barrels of oil are consumed per day. In Peru, the demand for crude oil is 175 thousand barrels per day, where only in the Peruvian Coast there is a demand of 70 % (Central Coast 42 %, South Coast 14 % and North Coast 14 %), the Jungle 9% and the highlands with 21 % (OSINERGMIN, 2017). During 2014 and 2016 there were multiple spills nationwide. A large part of these incidents came from the company Petroperu, where 15,756 barrels of oil were spilled and of which only 12,143 barrels were recovered, generating an affected area of 1,599,963.6 m^2 (Arévalo, 2017). Oil spills in bodies of water generate oxygen depletion, increased turbidity and decreased organic matter, causing aquatic species to be the most affected (Arenas, 2015).

Several studies related to hydrocarbon removal in water bodies employ natural adsorbents in contact times between 10 to 45 min in order to obtain reliable results that achieve hydrocarbon removal efficiencies above 90% (Salinas, 2010; Leiva et al., 2012; Salazar, 2012; Martínez et al., 2013; Zhang et al., 2013; Lazim et al., 2018; Villegas et al.,2017; Castillo, 2017; Domínguez, 2017; Zawrah et al., 2018; Díaz et al., 2018; Espino, 2018; Abanto, 2018; Flores et al., 2018; Zhou et al., 2019; García, Peñafiel and Rodríguez, 2019).

Sheep wool can be adapted to any form of application (heat or humidity) and has hygroscopic capacity that allows it to remove crude oil from bodies of water (Alonso, 2015). The crude oil removal capacity is achieved by identifying an absorbent and using a methodology based on the ASTM-F726 standard. Among the oil absorbent materials there are commercial synthetic absorbents made of polypropylene or polyurethane, whose main disadvantage is their inability to biodegrade. In contrast, natural sorbents are inexpensive and can biodegrade (Kamel and Sakhawy, 2011). Crude oil affects marine ecosystems by causing suffocation of algae and plants, poisoning of organisms by absorption or friction, death from toxic material (volatile organics) from oil in the water, destruction of the food source of species and destruction of the natural thermal insulation of animals (Sever, 2005).

The aforementioned research shows that the use of natural adsorbents for the removal of hydrocarbons in water bodies is totally efficient, decreasing water turbidity and removing more oil than other synthetic adsorbents. This

research allows the use of natural adsorbents for hydrocarbon removal. Therefore, the main objective was to determine the effect of the use of Assaf sheep wool in the removal of hydrocarbons (diesel) present in water bodies in a short time, and thus have a correct vision of its reuse as an alternative to counteract oil spills in water bodies, preventing the contaminants from spreading and affecting the flora and fauna.

2. Materials and methods

2.1 Obtaining and characterization of the diesel and the wool

The DB5 diesel was acquired from a commercial fuel sales stand in Lima, Peru. On the other hand, Assaf sheep wool was obtained during the shearing of sheep in the district of Pampachiri in the province of Andahuaylas, Apurimac, Peru.

The physical characteristics of the wool such as humidity, floatability, diameter, fineness, density and porosity were determined. The physical and chemical characteristics of the diesel were also determined, such as density, viscosity, API gravity and chemical elemental analysis (N, C, H, S and O).

2.2 Elaboration of the glass tanks and wool pads

Eight glass tanks were made, measuring 20 cm long, 15 cm wide and 15 cm high, were filled with 1 L of distilled water and 150 mL of diesel. The pads were made of tocuyo cloth, measuring 15 cm long and 10 cm wide, and were weighed prior to the experiment. Figure 1 shows the design of a glass tank (Figure 1-a), and a wool pad (Figure 1-b).
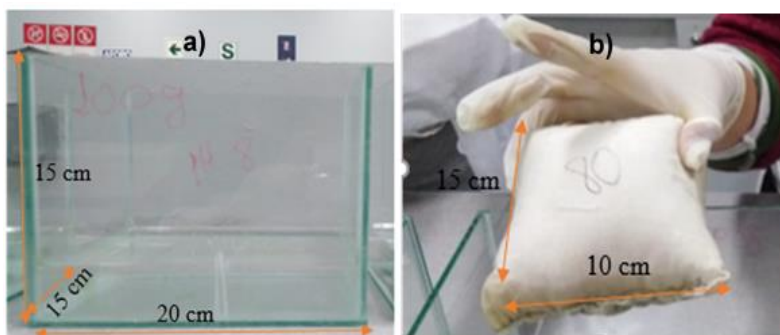

Figure 1: Dimensions: a) Glass tanks and b) Wool pads

2.3 Removal of hydrocarbons in water bodies

Hydrocarbon removal was performed using different doses of sheep wool (40, 60, 80, 100, 120, 140 and 160 g) at different pH values (4, 5, 6, 7, 8, 9, 11 and 12) and contact times (30, 60, 90, 120, 150, 180 and 210 s). All this was done to determine the optimum dose, optimum pH and optimum hydrocarbon removal time. The pH of the solution was adjusted with aliquots of dilute NaOH and HCl solutions, and the retention capacity was estimated using equation 1.

For removal, parameters such as pH, temperature, electrical conductivity, BOD, COD and total petroleum hydrocarbons (TPH) were evaluated.

All the tests for the parameters mentioned above were carried out in triplicate.

$$RC = \frac{W_i - W_d}{W_d} \tag{1}$$

Where: RC, retention capacity (%); W_i, impregnated natural sorbent (g) and W_d, dry natural sorbent (g)

3. Results and discussion

3.1 Characterization of wool and diesel

Table 1 details the physicochemical properties of the wool, showing a humidity of 16.48 %, a diameter of 36 μm, a true density of 0.19 g/cm³ and a porosity of 0.68 g/cm³.

Table 1: Physicochemical properties of wool

Wool characteristics	
Humidity (%)	16.48
Floatability	Si
Diameter (µm)	34
Fineness	Coarse
True density (g/cm³)	0.19
Apparent density (g/cm³)	0.06
Porosity (g/cm³)	0.68
Oil (%)	6.39

The elemental percentage and physical properties of the diesel are shown in Table 2. It shows that the commercial diesel meets the physical properties and has a carbon composition of 72.09 %.

Table 2: Physical properties of the hydrocarbon (diesel)

Hydrocarbon characteristics					
Density (kg/m³)			829.9		
Kinematic viscosity (cSt)			2.98		
API gravity			39.00		
Elemental analysis	%N	%C	%H	%S	%O
	0.12	72.09	11.59	<0.1	1.85

3.2 Removal of diesel as a function of pH, dosage and contact time

Table 3 shows the retention capacity of the absorbent (sheep wool) as a function of pH. It is observed that the best retention is achieved at pH 8, reaching a diesel removal of 91.72 %.

Table 3: Determination of optimum pH: contact time = 1 min

pH	Weight of 150 mL of diesel (g)	Amount of synthetic water (mL)	Dry natural sorbent (g)	Impregnated natural sorbent (g)	Total amount of diesel absorbed (g)	Retention capacity (%)
4	120	1000	60	112.74	52.74	87.90
5	120	1000	60	112.61	52.61	87.68
6	120	1000	60	112.03	52.03	86.72
7	120	1000	60	112.76	52.76	87.93
8	120	1000	60	115.03	55.03	91.72
9	120	1000	60	114.07	54.07	90.12
11	120	1000	60	114.15	54.15	90.25
12	120	1000	60	114.21	54.21	90.35

Table 4 shows the retention capacity of the absorbent as a function of the dose. At a dose of 120 g, the highest percentage of diesel retention is obtained, reaching a value of 92.31 %.

Table 4: Determination of the optimum dose: pH = 8 and contact time = 1 min

Dose (g)	Impregnated natural sorbent (g)	Total amount of diesel absorbed (g)	Retention capacity (%)
40	47.82	7.74±0.09	19.34±0.225
60	115.06	55.03±0.03	91.72±0.05
80	137.11	57.08±0.04	71.35±0.05
100	167.27	67.35+0.08	67.35±0.08
120	230.80	110.78±0.02	92.31±0.015
140	255.99	116.00±0.03	82.53±0.345
160	255.25	95.35±0.1	59.59±0.005

Table 5 shows the retention capacity of the absorbent as a function of contact time. It shows that the optimum time for diesel removal is 150 s, reaching a removal of 94.10 %, after which time there is a slight decrease in the absorbent's retention capacity.

Table 5: Determination of optimum time: pH = 8 and adsorbent dosage = 120 g

Time (s)	Dry natural sorbent (g)	Impregnated natural sorbent (g)	Total amount of diesel absorbed (g)	Retention capacity (%)
30	120	154.67	33.67±0.04	28.05±0.035
60	120	230.80	110.78±0.02	92.31±0.015
90	120	230.90	110.84±0.09	92.40±0.04
120	120	231.65	111.67±0.03	93.05±0.025
150	120	232.92	112.92±0.04	94.10±0.03
180	120	231.99	111.95±0.1	93.29±0.01
210	120	228.76	108.76±0.05	90.63±0.04

Different investigations also used natural sorbents, among them, Domínguez (2017) achieved a diesel removal of 44.33 % using 100 g of chicken feathers, in a time of 2 min. Likewise, Espino (2018) determined that human hair adsorbs 67.33 g of oil in 8 min and chicken feathers adsorbs 102.0 g of oil in 5 min, while Pablo (2010) determined that chicken feather meal adsorbs 2.60 g of hydrocarbon in 5 min. In contrast, Castillo (2017) showed that sugarcane bagasse adsorbs 10.9 g of oil in 45 min and *Luffa cylindrica* adsorbs 8.70 g of oil in 30 min. Similarly, Leiva et al. (2012) and Diaz et al. (2018) used sugarcane bagasse as a natural adsorbent, achieving retention capacities greater than 80% in an optimum time of 24 hours. Abanto (2018) used coconut fiber as a natural adsorbent, obtaining adsorptions of 93.93 % and 85.88 % for kerosene and gasoline, respectively. For their part, Garcia et al. (2019) applied a mixed culture of hydrocarbon degrading microorganisms such as *Acinetobacter sp.*, *Pseudomonas sp* and *Mycobacterium sp*, obtaining a maximum removal of 92 % in the third week of treatment.

All the above mentioned investigations had good hydrocarbon removal results using natural sorbents. Similarly, in this research it is demonstrated that Assaf sheep wool had efficient results in oil removal, and it is also an innovative, economical, easily accessible method that induces reuse and can help counteract the environmental problems of oil spills in water bodies.

3.3 Characterization of the synthetic sample both before and after treatment

The synthetic sample initially presented a temperature of 24.9 °C, electrical conductivity of 633 µS/cm, pH 8, BOD of 800 mg/L, COD of 1700 mg/L and TPH of 750 mg/L. After treatment, variations were observed in the parameters studied, as shown in Table 6. It was observed that at a contact time of 150 s, the best reductions in BOD, COD and TPH were obtained, with values of 171 mg/L, 234 mg/L and 52 mg/L, respectively. This

indicates that treatment with sheep wool not only removes hydrocarbons but also improves the physical, chemical and organic properties of the water.

Table 6: Physical, chemical and organic characteristics of synthetic water after treatment with wool pads

Time (s)	Temperature (°C)	Electrical conductivity (µS/cm)	pH	BOD (mg/L)	COD (mg/L)	TPH (mg/L)
30	23.8±0.1	567±1	7.8±0.1	446±2	805±2	266±1
60	23.9±0.1	542±1	7.9±0.1	424±1	785±2	215±1
90	23.9±0.1	504±1	7.9±0.1	379±3	631±3	127±3
120	23.7±0.1	500±1	7.9±0.1	324±3	551±2	87±3
150	23.7±0.1	564±1	7.9±0.1	171±3	234±3	52±3
180	23,7±0.1	505±1	7.9±0.1	335±1	545±3	94±1
210	22.8±0.1	576±1	8.0±0.1	289±2	426±3	81±1

4. Conclusions

The research showed that Assaf sheep wool is a good bioadsorbent of hydrocarbons (diesel) and could be applied in water bodies contaminated with these compounds. Assaf sheep wool had a humidity of 16.48 %, a diameter of 34 µm, a true density of 0.19 g/cm^3, and a porosity of 0.68 g/cm^3. On the other hand, the optimum dose of Assaf sheep wool for the retention of hydrocarbons in the water bodies was 120 g, reaching a removal percentage of 94.10 % in a contact time of 150 s and at a pH value of 8.

Acknowledgments

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