EVALUATION OF NATURAL SORBENT MATERIALS FOR CLEANING OF OILY WATERS[1]

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Abstract

Despite the great concern about the environment and a growing search for sources of clean and renewable energy and raw materials, there is a great and increasing demand for the use of crude oil and it's derivatives. Water and oil are in contact in various industrial processes, whether directly connected to the extraction and refining of crude oil or not. Even with all care in the separation between water and oil, spills may occur and there is a need for research to contain or clean up polluted ecosystems. Even though oil is immiscible with water, in practice it is very common to find it in the form of emulsion what has been considered a complicating factor both technically and financially to various industries in various sectors. Effluents must be discarded according to the legislation. The aim of this work is to create a simple, fast and efficient method of cleaning oily water. Oil and used mineral insulating oil were tested in dry sorption system (water-free) and in stirred aqueous systems with natural woven fibers used as sorbent materials and compared to a commercial product of polypropylene in the form of mats. Two types of fibers were tested, vegetable (chorisia speciosa) and animal (white poodle fur and a mixture of dog fur from different dog breeds), waste of establishments that provide care to animals. The mixture of dog fur was statistically representative of the samples obtained in pet shops.

Key words: Sorbent; oily waters; Insulating Mineral Oil; Crude Oil.

1 INTRODUCTION

Even with all care in the separation between water and oil, eventually, spills still occur and it makes necessarily researches to contain oil or clean polluted ecosystems. When a spill occurs it is necessary to establish an emergency management plan which defines how cleaning will take place.

Mechanical, physical, chemical and biological agents can be used to recover, remove or degrade the oil. However, the mechanisms of sorbents oil recovery are one of the most used in cases of oil spills in the marine environment (WEI et al, 2003; and RIBEIRO RUBIO, 2000).

The contaminant component of water can have different origins: from effluents from oil refineries and metallurgical industries to the municipal water networks, represented by the cesspool of human and kitchens, which contains average levels between 9 and 30% lipid (QUEMNEUR and Marty, 1994), additionally the waste of engines, machines, parts and cars washing, workshops effluent and gas stations (Mysore et al., 2005).

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The maintenance shops have a washing area where the equipment is clean, generating effluents containing oils, which serve to an oil and grease separator box where the oil is removed in the process of cleaning (actually every six month) and collected by a specialized firm responsible for its proper disposal (SANTOS, 2006). The disposal of produced water for the environment in Brazil is governed by Resolution 357 of CONAMA, which sets limits on contaminants in wastewater. In the case of oil and grease, this limit is 20ppm (mg / l) for oil and 50ppm for vegetable oils and animal fats.

According Annunciado et al, a material to be used as sorbent must have oleofilic and hydrophobic characteristics, ie have the ability to attract oil and repel water. Natural products have the advantage of low cost, biodegradability and abundance. Using discarded materials for applications in natural cleaning oil spill and / or the purification of oily waters may represent an attractive alternative economically, and is an environmentally desirable practice (Adebajo, 2003).

This study aims to test how natural sorbent materials currently discarded can be woven and used in cleaning of oil spills (with woven mats). It was tested two types of fiber, vegetable (chorisia speciosa or sil-floss) and animal (white Poodle fur and a mixture of several dog fur of defferent breeds), scrap pet shops. Initially, it was produced yarn with the three alternative materials, and then the carpets were woven by hand for the sorption tests where sorption capacity of each material was evaluated.

2 MATERIAL AND METHODS

2.1 MATERIALS

2.1.1 NATURAL FIBER AND COMMERCIAL SORBENTS

Chorisia speciosa (silk-floos) was obtained from local trees and the fur of white poodle was collected after clipping, and both of the materials were made into yarn without been washed.

The hair of various dog breeds was donated each week by Pet Shop ALFADOG during the period 20/12/2009 to 24/10/209. After collection, they were statistically analyzed relating the mass concentration with the occurrence of the race. After that, they were processed into yarn without been washed to be twisted. As a comparison base, it was used a commercial sorbent based on polypropylene.

2.1.2 PETROLEUM AND MINERAL OIL

The petroleum used in the sorption tests was donated by PETROBRAS Business Group, Getúlio Vargas Refinery (REPAR).

The insulating oil used was donated by ELETROSUL.

2.2 METHODS

2.2.1 CHARACTERIZATION OF MINERAL INSULATING OIL AND PETROLEUM.

The viscosity of the insulating mineral oil used was determined by ASTM D445-94 NBR-10441-2007 to 40 º C, through the use of a capillary with the aid of a bath thermostatic brand model DAIRY ASTM D445-94 with microprocessor controller JULABO MC at the ELETROSUL Physical Chemistry Laboratory. The two standards are equivalent and recommended for physico-chemical mineral insulating oil, as the resolution Resolution ANP N º 36, DE 5.12.2008 - published in the Official Gazette on 8.12.2008.

2.2.2 GATHERING AND STATISTICALS OF THE DOG'S HAIR FROM DIFERENT BREEDS

From 48 samples collected from different races totaling 1119.6 g it was found the statistical proportion of each race in mass with respect to the total mass obtained and the occurrence of the dirty or clean. Races were analyzed: Lhasa Apso, Maltese, Poodle, Saint Bernard, Schamauzer, Shitsu and York Shire. The dog fur was spun without any treatment to avoid any change from the gathering condition.

2.2.3 PREPARATION OF THE MATERIALS IN FORM OF SORBENTS MATS FOR SORPTION TESTS

The commercial sorbent, supplied in the form of mats, was cut in circular diameter of 1.5 cm (1d figure). The plants and animals sorbent, to be prepared in mat form, needed to be processed through spinning and manually twisted into small rugs. For wiring, the first step was to separate and guide the fibers into small strips about 20cm, then the strips were crushed with the help of a plastic that facilitated the process of twisting.

The strips were attached along the process of twisting and then rolled into a ball. The wires obtained in this process were approximately 0.5 g / m weight. The balls used for the formation of small braided rugs had to be stored for a minimum of 3 days, otherwise the wires wouldn't stand the manufacturing process of the rugs. It was used the *crochet* technique to braid wires and form carpets round 1.5 cm diameter.

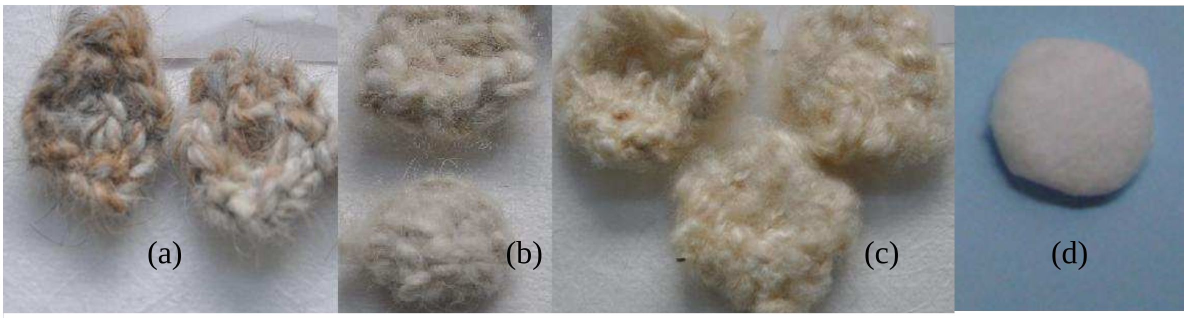

Figure 1. Carpets: several breeds of dog's hair (a), hair Poodle (b), chorisia speciosa (c) and commercial sorbent

2.2.4 DRY STATIC SORPTION IN PETROLEUM TEST

Dry static sorption test consists in putting in contact the materials to be tested, in this case petroleum and the sorbent materials. Previously weighted in analytical balance (Bioprecisa), the sorbent materials were introduced in a beaker with 10 ml of oil.

The tests were performed in 5, 15, 30 and 60 minutes. After the time immersed in oil the samples were placed in a sieve to drain the oil not retained during15 minutes. It was used for each of the times triplicate samples of kapok (*Chorisia speciosa*), white Poodle fur braided, hair of various dog breeds and mixture of dog fur. Then the samples were weightened in analytical balance using glass plates.

The sorption was expressed in the form of amount of oil sorbed by dry mass of material (S0) sorbent as shown in the equation: $S = (S_t - S_0) / S_0$, where S_t is the total mass of sorbed. Thus, the sorption is given in units of g oil / g of dry sorbent.

2.2.5 DRY STATIC SORPTION IN USED MINERAL INSULATOR OIL TEST

Dry static sorption in used insulator oil test was conducted in the same way as for the dry static sorption in petroleum test.

3 RESULTS

3.1 GATHERING AND STATISTICS OF DOG'S HAIR FORM DIFERENT RACES

From 1119.6 g of dog's hair only 77.8g was washed before the clipping. What determines the washing before de clipping is the size of the dog: for big dogs the clipping is made without washing it. It was analyzed the mass relation of each dog race in comparison of the total amount of hair gathered.

Table 1. Percentage mass of each breed for the total mass

Race	Mass (g)	%
Lhasa Apso	467,7	42
Maltês	78,4	7
Poodle	205,4	18
St. Bernard	21,2	2
Schamauzer	152,6	14
Shitzu	36,6	3
York Shire	157,7	14

It was not analyzed the color statistics due to the difficult of determining the right proportion, once the great part of the dogs had more than one color.

3.2 DRY STATIC SORTION IN PETROLEUM TEST

Considering the permanency of the samples in the oil, the following results were found as show below:

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Table 2. Sorption capacity in petroleum of mat samples made of mixture of dog fur

Time	Number	S_0	S_t	$S = (S_t - S_0)/S_0$	Average g oil/g sorbent
5 min	**1**	0,11	0,74	5,50	5,66
	2	0,16	1,09	5,96	
	3	0,11	0,73	5,53	
15 min	**11**	0,16	1,02	5,27	5,26
	12	0,17	1,00	4,99	
	13	0,13	0,82	5,52	
30 min	**21**	0,13	0,73	4,57	4,63
	22	0,14	0,97	5,95	
	23	0,25	1,09	3,38	
60 min	**31**	0,14	0,75	4,47	4,76
	32	0,13	0,98	6,32	
	33	0,36	1,59	3,48	

Table 3. Sorption capacity in petroleum of mat samples made of Poodle fur

Time	Number	S_0	S_t	$S = (S_t - S_0)/S_0$	Average g oil/g sorbent
5 min	**4**	0,12	0,98	7,45	7,78
	5	0,11	1,02	7,99	
	6	0,09	0,84	7,90	
15 min	**14**	0,22	1,46	5,59	6,68
	15	0,12	1,03	7,70	
	16	0,11	0,87	6,76	
30 min	**24**	0,08	0,79	8,87	9,39
	25	0,08	0,98	11,29	
	26	0,12	1,08	8,02	
60 min	**34**	0,11	0,89	6,93	6,72
	35	0,12	1,01	7,55	
	36	0,14	0,94	5,68	

Table 4 Sorption capacity in petroleum of mat samples made of *Chorisia speciosa*

Time	Number	S_0	S_t	$S = (S_t - S_0)/S_0$	Average g oil/g sorbent
5 min	**7**	0,03	0,38	9,96	10,49
	8	0,05	0,64	12,66	
	9	0,16	1,61	8,85	
15 min	**17**	0,31	2,52	7,15	8,22
	18	0,10	0,90	8,36	
	19	0,18	1,82	9,15	
30 min	**27**	0,04	0,48	11,17	9,30
	8	0,18	1,65	7,98	
	29	0,18	1,76	8,75	
60 min	**37**	0,04	0,52	12,05	8,99
	38	0,34	2,58	6,51	
	39	0,21	1,96	8,40	

Table 5. Sorption capacity in petroleum of mat samples made of PP commercial sorbent

Time	Number	S_0	S_t	$S = (S_t-S_0)/S_0$	Average g oil/g sorbent
5 min	**10**	0,11	0,99	7,74	7,34
15 min	**20**	0,12	0,98	7,12	
30 min	**30**	0,15	1,23	7,05	
60 min	**40**	0,11	0,97	7,45	

3.3 DRY STATIC SORTION IN MINERAL OIL TEST

Considering the permanency of the samples in the mineral oil, the following results were found as show below:

Table 6. Sorption capacity in mineral oil of mat samples made of a mixture of dog fur

Time	Number	S_0	S_t	$S = (S_t-S_0)/S_0$	Average g oil/g sorbent
5 min	**41**	0,09	0,60	5,76	5,09
	42	0,10	0,59	4,68	
	43	0,10	0,61	4,83	
15 min	**51**	0,07	0,46	5,90	5,07
	52	0,08	0,45	4,37	
	53	0,08	0,45	4,92	
30 min	**61**	0,10	0,62	5,43	5,07
	62	0,15	0,93	5,02	
	63	0,11	0,61	4,76	
60 min	**71**	0,09	0,58	5,28	4,95
	72	0,13	0,82	5,35	
	73	0,19	0,99	4,22	

Table 7. Sorption capacity in mineral oil of mat samples made of Poodle fur

Time	Number	S_0	S_t	$S = (S_t-S_0)/S_0$	Average g oil/g sorbent
5 min	**44**	0,36	1,97	4,47	4,12
	45	0,33	1,81	4,43	
	46	0,38	1,70	3,46	
15 min	**54**	0,27	1,55	4,68	4,29
	55	0,23	1,25	4,52	
	56	0,39	1,84	3,68	
30 min	**64**	0,28	1,44	4,23	4,27
	65	0,32	1,44	3,44	
	66	0,22	1,36	5,14	
60 min	**74**	0,07	0,60	8,09	5,29
	75	0,48	2,31	3,80	
	76	0,38	1,92	3,99	

Table 8. Sorption capacity in mineral oil of mat samples made of *Chorisia speciosa*

Time	Number	S_0	S_t	$S = (S_t-S_0)/S_0$	Average g oil/g sorbent
5 min	**47**	0,02	0,36	16,84	12,67
	48	0,03	0,34	12,15	
	49	0,17	1,72	9,02	
15 min	**57**	0,03	0,33	9,28	7,89
	58	0,15	1,42	8,28	
	59	0,31	2,21	6,11	
30 min	**67**	0,03	0,36	10,67	9,50
	68	0,27	2,53	8,30	
	69	0,22	2,27	9,54	
60 min	**77**	0,03	0,45	12,46	11,02
	78	0,19	2,26	11,06	
	79	0,16	1,70	9,54	

Table 9. Sorption capacity in mineral oil of mat samples of a PP commercial sorbent

Time	Number	S_0	S_t	$S = (S_t-S_0)/S_0$	Average g oil/g sorbent
5 min	**50**	0,08	0,61	6,46	6,04
15 min	**60**	0,11	0,69	5,22	
30 min	**70**	0,10	0,70	5,91	
60 min	**80**	0,09	0,66	6,59	

3.4 PRELIMINARY DINAMIC SORTION TEST IN WATER

The samples were weightened before the imersion in the stirred oil / water system. The silf-flossk (chorisia speciosa) and the white Poodle fur removed almost all the petroleum in the water surface before the end of the test time and still had some clean areas that weren’t put in contact during stirring.

The samples made of yarns from the mixture of dog fur did not clean the oil from water and were completely soaked with oil after its withdrawn. Further tests are being conducted to evaluate the sorption capacity of these materials in systems with smaller samples and with filter systems.

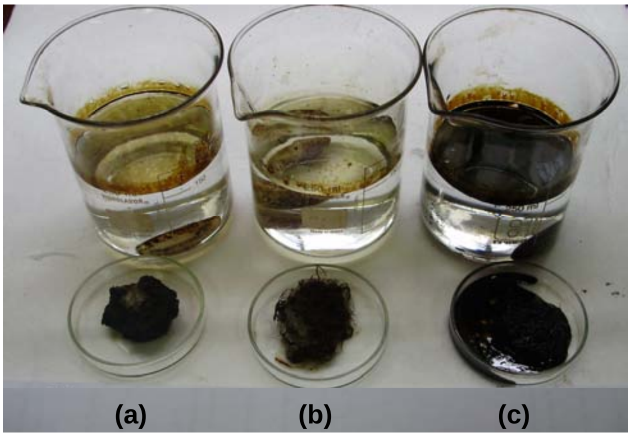

Figure 2. Samples after the sorption of Petroleum in dynamic system: chorisia speciosa (a), hair Poodle (b) and mixture of hair dog fur (c)

Analyses are being conducted using distillation to evaluate the amount of water absorbed during the aqueous tests of the three materials. Also, the stirring of the aqueous systems must be better controlled in order to put the whole sorbent material in contact with the liquid. Also, it was observed that thinner threads produce more flexible woven mats that can more easily be in contact with the liquid medium and therefore, have a higher sorption capacity.

4 DISCUSSION

The higher amount of dog fur in the samples collected from different races came from the Lhasa apso breed.

Dry oil sorption with the white poodle mats showed better sorption capacity results than the commercial PP mat sorbent.

The silk-floss mats showed the best results concerning sorption capacity in all tests, even surpassing the commercial sorbent.

According to Perotta, the coat of white poodle has better results as sorbent with less viscous oils. Thus, it is expected that this material presents higher sorption capacity in aqueous systems with vegetable and light mineral oil spills.

The difficulty in manually produce a thread with a uniform thickness may have contributed to the close results between the sorbent produced with the mixture of dog fur and the commercial PP mat sorbent.

Samples with lower weight were samples made from thinner threads, and these ones presented higher values of oil sorption (in grams). The possibility of spinning silk-floss and dog hair from the disposal of pet shops is a good alternative for the production of woven mats with the purpose of use them as sorbent material for oil spills in water or dry environments.

5 CONCLUSIONS

The results showed that despite the fact that there is no commercial machines to make threads and woven mats from silk-floss and dog fur, it is possible to do it manually. Considering that these materials can be used as efficient oil sorbents, adjustments in the commercial machines can be made in order to make it possible the weaving of these materials into threads and then woven mats. Tests in aqueous medium show the higher efficiency of woven mats made of silk-floss and Poodle fur in clean water containing oil spills. All materials tested were more efficient as sorbents for petrolum or mineral insulating oil in dry environment than the commercial polypropylene sorbent. Additional tests should be conducted to determine the level of water absorbed in the aqueous sorption tests. The use of natural materials in this study represents economically advantageous contribution for cleaning oily waters and oil spills.

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REFERENCES

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS – NBR 10441 Produtos de petróleo – Líquidos Transparentes e Opacos – Determinação da Viscosidade Cinemática e Cálculo da Viscosidade Dinâmica, 2007.

ADEBAJO, M.O., FROST, R. L. Acetylation of raw cotton for oil spill cleanup application: na FTIR and C MAS NMR spectroscopic investigation. Australia, 2003.

ANNUNCIADO, T. R. Estudo da *Chorisia speciosa* e outras fibras vegetais como sorvente para o setor do Petróleo. Pós-Graduação em Engenharia e Ciência dos Materiais. Universidade Federal do Paraná, Curitiba, 2005.

AMERICAN SOCIETY FOR TESTING AND MATERIALS Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation D95-83. Annual Book of ASTM Standards. Printed in Philadelphia, PA, USA 1990.

Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity) Annual Book of ASTM Standards. Printed in Philadelphia, PA, USA 2004.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS

CONSELHO NACIONAL DO MEIO AMBIENTE-CONAMA RESOLUÇÃO No 357, DE 17 DE MARÇO DE 2005

MYSORE, D.; VIRARAGHAVAN, T.; JIN, Y. Treatment of oily waters using vermiculite. Water Research 39, p. 2643-2653, 2005.

PEROTTA, L. Avaliação de Diferentes Tipos de Recheios em Colunas de Adsorção para Purificação de Águas Oleosas. Universidade Federal do Paraná, Curitiba, 2009.

QUEMNEUR, M.; MARTY, Y. Fatty acids and sterols in domestic wastewaters. Water Research 28, p. 1217–1226, 1984.

RIBEIRO, Tânia H.; SMITH, Ross W.; RUBIO, Jorge . Sorption of Oils by the Nonlinving Biomas s of a Salvínia sp. Environmental and Science Technology. v. 34, n. 24 ,p. 5201-5205, 2000.

SANTOS, Isadora.Rodrigues. Elaboração de Programa de Gestão Ambiental para a Unidade Eletrosul Sertão do Maruim - São José - Setores OFCEN e LALTE. Seminário de Manutenção da Eletrosul. Campo Grande, 2006.

SANTOS, J., SANTOS, L. P. Avaliação de Fibras de Resíduos de Agave Azul como Material Sorvente para o Setor do Petróleo. Universidade Federal do Paraná, Curitiba, PR, 2008.

WEI, Q.F., MATHER, R.R., FOTHERINGHAM, A.F. & YANG, R.D. Evaluation of
nonwoven polypropylene oil sorbents in marine oil-spill recovery. Marine Pollution Bulletin, v. 46, n.6, p.780-783, 2003.