STUDY OF SORPTION PROPERTIES OF LIGNIN-DERIVATIZED FIBROUS COMPOSITES FOR THE REMEDIATION OF OIL POLLUTED RECEIVING WATERS

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The sorption properties of lignin-wool composites towards oil pollution at different concentrations of the contamination were studied. The release ability of oil pollutant was studied by a gravimetric method and by determining the chemical oxygen demand of cleaned water. It has been established that technical hydrolysis lignin–wool composites display a low release ability of oil-based pollutants and a slow rate for achieving release equilibrium.

Keywords: Technical hydrolysis lignin, Wool shoddy, Sorbent, Oil pollution of water, Release equilibrium

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INTRODUCTION

Oil spills that occur from river-going vessels, in ports, and from manufacturing facilities adjacent to rivers are an exceptionally great ecological problem. Nowadays, the ecological protection against oil pollution is being carried out in different ways and means, depending on the kind, the composition, and the location of the pollution.

A number of papers (Masahiro 1994; Fletcher 1994; Davis 1994) are related to using biological means for cleaning waters, but these methods are not applicable for typical situations. In those cases the use of highly effective fibrous-polymer sorbents may be of great importance.

Papers and patents are available that deal with highly fibrillated fibrous materials for cleaning failing protein water (Chem 1998), micro-fibrous sorbents on the basis of thermoplastic polymers (Eur. Patent Appl. EP0608884 1994), and wool fibrous materials of high surface area for cleaning of oil spills in the Persian Gulf in 1990 (Ronald 1993). Testing of wood saw dusts for the cleaning of water surface from average oil spills (Hianov 1995), preparation of highly effective sorbents on the basis of fibrous waste from paper production (Kugin 1994), and the use of lignin-containing waste for cleaning water (Grigoriev 1996) have also been reported.

The possibilities for cleaning oil pollution by sorbents on the basis of fibers, polymer, and wood, however, have not been well investigated. Good remediation of oil-polluted water can be achieved with wood-fibrous sorbents, and in particular with fibrous and lignin-containing materials due to their high sorption capacity towards oil, oil products, and heavy metals. These fibrous and lignin-containing materials are cheap, as well as being waste products with high sorption ability. Of special interest in this respect are the wool shoddy (WS) and technical hydrolysis lignin (THL). These materials possess highly developed surfaces, which together with different functional groups determine their high sorption ability. Technical hydrolysis lignin (THL), synthetic fabrics, or fibrous wastes from their production are used for collection of oil and lubricants from water and soil (Russian Patent RU2049543 1995).

The sorption of lignin under dynamic turbulent conditions has been investigated. The increasing of the degree of turbulence leads to a higher sorption rate and velocity. The rate and velocity of sorption depends on the ratio of oil product to lignin. Two technological schemes for the remediation of oil-polluted water with hydrolyzed lignin have been developed (Finland Patent FI912863 1992).

The criteria necessary to achieve selection of suitable sorbents for the remediation of polluted water are not only the initial and final sorption capacity but also the ability for retention of the oil pollutants, i.e., it must possess a low desorption rate.

Data on the ability of lignin and textile fibers to retain of oil pollutants once the sorption equilibrium has been reached has not been reported. Therefore, the release equilibria at different concentrations of oil pollutants have not been previously investigated. The determination of such a correlation would be of great practical importance for remediation oil spills that possess different thicknesses on a receiving water surface.

The purpose of the present investigation is to provide a study of the release characteristics of oil pollutants of wood - fibrous composites based on lignin and wool shoddy at different contamination concentrations.

EXPERIMENTAL

Materials

All work was conducted with the following materials:

- Technical hydrolysis lignin (THL), obtained by acid hydrolysis of wood in industry and situated in 2001 year near the town Razlog, Bulgaria. The size fraction with 0.125-0.315 mm was used in the present study.
- Fibrous waste materials (the so-called wool shoddy (WS) consisted of 50 weight percent wool, 25 weight percent viscose, and 25 weight percent polyamide)

The ratios of THL:WS were 50:50; 75:25 and 90:10.

A crude oil with 0.85 g/ cm^3 specific weight and pH 7 was used for oil pollution at a ratio of oil to water of 10:0 (100 weight% oil), 6:4 (60 weight % oil), and 4:6 (40 weight % oil).

Techniques

Two methods to study release characteristics have been developed:

1. Weight method for the determination of oil flow

Desorption properties were investigated at constant temperature (20^{o}C). A glass tube with diameter d=25 cm and height h=55cm was used. Wood-fibrous material (THL/WS) was put into the tube, and then the oil or mixture of oil/water was poured on.

The oil released quantity was measured during 270 min at regular intervals after a 15 min waiting time for obtaining the maximal sorption of oil pollution.

2. Chemical Oxygen Demand (COD) testing

The release of bound oil was determined by Chemical Oxygen Demand (COD) testing. The COD was ascertained by using potassium dichromate, a well known method for the assessment of the concentration of organic pollutants. 50 ml of water was poured into the THL with WS that was in the glass tube after completion of the desorption process as described above (weight method). After one minute, water was drawn out for the next 5 minutes. This process was repeated until release equilibrium (flowing of clear water out of the tube) was achieved. The COD of the oil-containing fractions was then determined.

RESULTS AND DISCUSSION

The experimental data corresponding to the release of the oil pollutants from a lignin-fibrous mixture (THL:WS-50:50) at three ratios of oil to water, are shown in Fig.1. It can be seen from Fig. 1 that the release at 100 % (10:0) oil pollutant concentration was steady, and the release equilibrium was reached after 240 minutes.

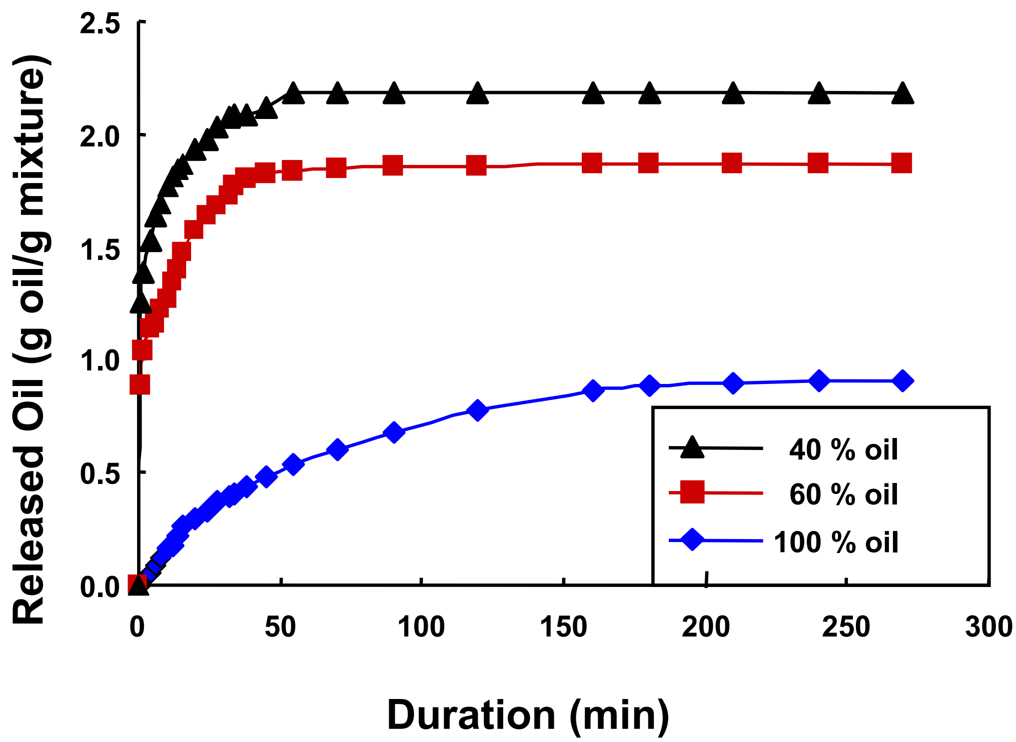

Fig.1. Released quantity of oil by THL:WS (50:50) at different ratios of oil:water

At the ratios 6:4 and 4:6 oil to water it was seen that initially only water release occurred from the mixture (7 min for 60 % oil and 10 min for 40 % oil). The release equilibrium was reached after 240 minutes at 100 % oil and after only 60 min at 40 % oil. 100 % retention of oil pollutants was observed at the ratio 4:6. Therefore, the composite mixture of THL/WS – 50:50 is expected to be very suitable for use as a sorbent in the case of oil spills having low oil concentration.

The dependence of oil released quantity on lignin-fibrous composite (THL/WS-75/25) at three ratios of oil:water over 260 min is given in the Figure 2. The data show that the process of release of oil at 100 % oil pollution was rapid up to 60 minutes, and afterwards was steady. The equilibrium at the other ratios was reached very quickly, i.e., after approximately 30 minutes.

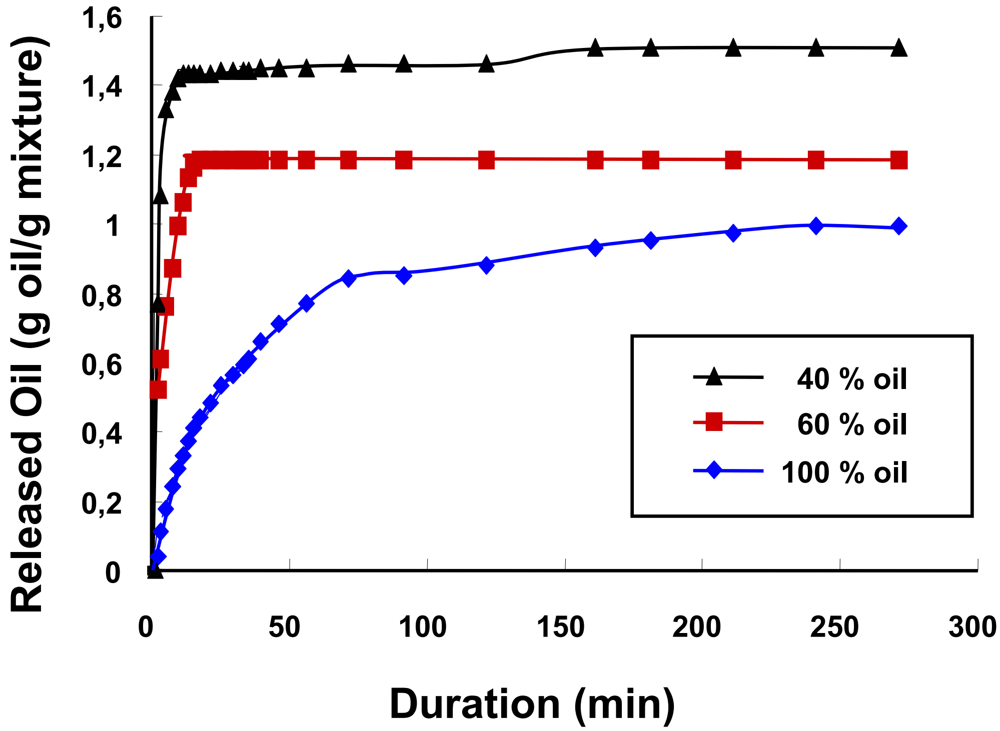

Fig. 2. Released oil quantity by THL:WS (75:25) at different oil percentage fractions

The data for the composite of 90 %THL and 10 % WS demonstrates the following dependencies:

- the release equilibrium was reached very quickly (38 minutes),
- initial water release was not observed, and
- released oil quantities at the three ratios of oil to water (10/0, 6/4, 4/6) were similar (Fig. 3).

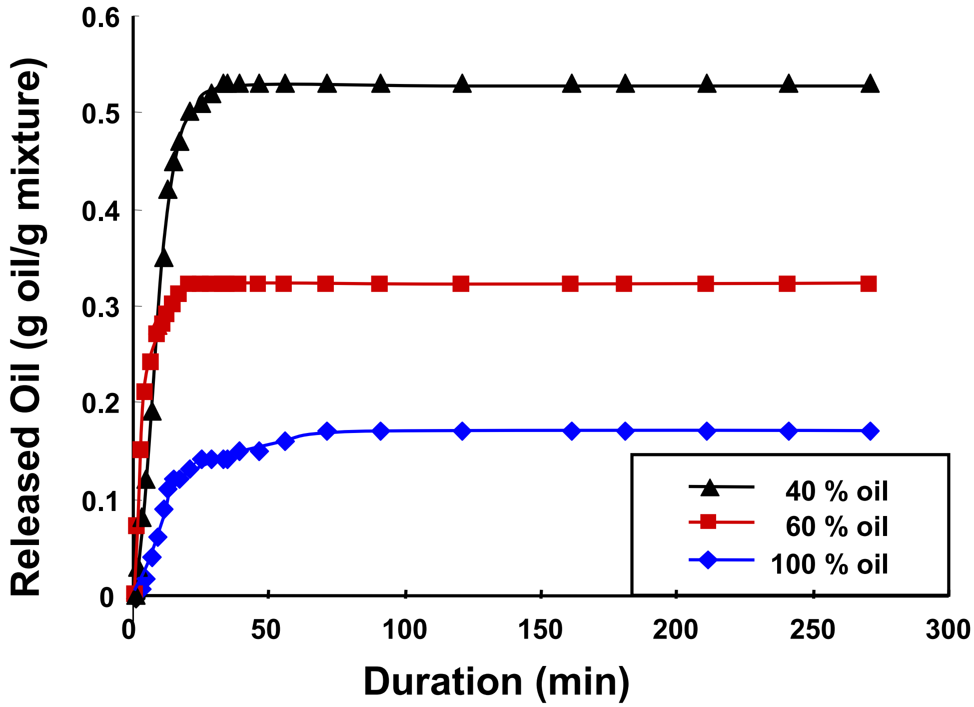

Fig. 3. Released oil quantity by THL:WS (90:10) at different oil percentages

Undoubtedly, these findings can be attributed to the favorable influence of the two components in the composites with the highest content of lignin. The WS gave higher maximal sorption, but THL displayed a higher capacity to retain the oil.

The established dependencies were confirmed from the results of the retained oil quantities at the three ratios of oil to water (Table 1).

A summary of the previous dependences is as follows:

- It is observed that there was a gradual decrease of the initial sorption capacity of composites when the level of WS ranged from 50 % to 10 %;
- The release process was similar at the three ratios of THL to WS;
- The release process of the three composites at the ratio of oil/water (6:4) was similar, but there were significant differences for the ratio of oil to water (4:6);

Therefore, it can be concluded that the THL/WS composites have significant advantages over the separate use of the two components in the process of release of oil

The data for COD, characterizing the sorption in different batches of materials, at the three ratios of oil/water - 10:0; 6:4; 4:6, are presented in Figs. 4, 5, and 6. The dependencies were similar to those for the physical desorption, as determined by the weight method.

The average rate of release was determined on the basis of the COD data. By washing water from the sorbent, the oil situated in the capillary system, i.e. connected by sorption process occurring during the pour and partially by physical adsorption, was separated. The contamination of this rinse water was determined by COD analysis.

Table 1. Oil, Retained Quantity (g oil/g mixture)

Duration (min)	THL:WS – 50:50			THL:WS – 75:25			THL:WS – 90:10		
	100 %	60 %	40 %	100 %	60 %	40 %	100 %	60 %	40 %
0.0	4.53	4.81	5.15	3.00	3.72	3.99	3.19	3.29	3.54
0.5	4.53	4.18	4.35	3.00	3.31	3.57	3.12	3.28	3.52
1.0	4.53	3.93	3.91	2.97	3.20	3.22	3.03	2.22	3.51
1.5	4.52	3.81	3.84	2.94	3.15	3.02	2.99	2.17	3.48
2.0	4.51	3.77	3.78	2.92	3.11	2.91	2.95	2.14	3.46
3.0	4.48	3.73	3.71	2.88	3.03	9.72	2.88	2.10	3.45
4.0	4.46	3.37	3.64	2.85	2.96	2.66	2.82	2.08	3.42
5.0	4.44	3.66	6.58	2.83	2.86	2.62	2.74	2.07	3.40
6.0	4.43	3.62	3.53	2.80	2.85	2.61	2.73	2.05	3.35
7.0	4.42	3.62	3.51	2.78	2.78	2.59	2.67	2.04	3.30
8.0	4.40	3.59	3.48	2.76	2.73.	2.57	2.62	2.02	3.26
8.5	4.39	3.58	3.45	2.75	2.70	2.57	2.60	2.02	3.24
9.0	4.39	3.57	3.43	2.74	2.69	2.57	2.59	2.01	3.22
9.5	4.38	3.56	3.41	2.73	2.68	2.56	2.58	2.01	3.21
10.0	4.37	3.54	3.40	2.72	2.66	2.56	2.57	2.01	3.19
10.5	4.37	3.53	3.39	2.71	.2.64	2.56	2.55	2.00	3.18
11.0	4.36	3.52	3.38	2.70	2.63	2.56	2.53	2.00	3.15
11.5	4.35	3.50	3.37	2.70	2.61	2.56	2.52	2.00	3.14
12.0	4.35	3.47	3.36	2.69	2.59	2.56	2.50	2.00	3.12
12.5	4.35	3.46	3.35	2.69	2.58	2.56	2.49	2.00	3.11
13.0	4.35	3.44	3.34	2.68	2.57	2.56	2.49	2.00	3.09
13.5	4.35	3.42	3.33	2.67	2.57	2.56	2.48	2.00	3.09
14.0	4.33	3.41	3.32	2.66	2.56	2.56	2.48	1.99	3.09
14.5	4.33	3.39	3.31	2.66	2.55	2.56	2.47	1.99	3.08
15.0	4.32	3.37	3.31	2.65	2.54	2.56	2.46	1.99	3.08
16.0	4.31	3.34	3.30	2.64	2.54	2.56	2.46	1.98	3.07
17.0	4.29	3.32	3.28	2.63	2.54	2.56	2.46	1.98	3.07
20.0	4.26	3.24	3.24	2.60	2.54	2.56	2.46	1.97	3.04
24.0	4.24	3.17	3.19	2.57	2.54	2.55	2.46	1.97	3.03
26.0	4.23	3.15	3.16	2.55	2.54	2.55	2.46	1.97	3.02
28.0	4.21	3.13	3.14	2.54	2.54	2.55	2.46	1.97	3.02
34.0	4.16	3.04	3.09	2.50	2.54	2.55	2.46	1.97	3.01
38.0	4.14	3.01	3.08	2.46	2.54	2.54	2.46	1.97	3.01
50.0	4.08	2.98	3.02	2.40	2.54	2.54	2.46	1.97	3.01
70.0	4.02	2.96	2.99	2.31	2.54	2.53	2.46	1.97	3.01
100.0	3.93	2.95	2.99	2.27	2.54	2.53	2.46	1.97	3.01
140.0	3.84	2.95	2.99	2.25	2.54	2.48	2.46	1.97	3.01
180.0	3.75	2.94	2.99	2.21	2.54	2.48	2.46	1.97	3.01
240.0	3.66	2.94	2.99	2.15	2.54	2.48	2.46	1.97	3.01
270.0	3.66	2.94	2.99	2.15	2.54	2.48	2.46	1.97	3.01

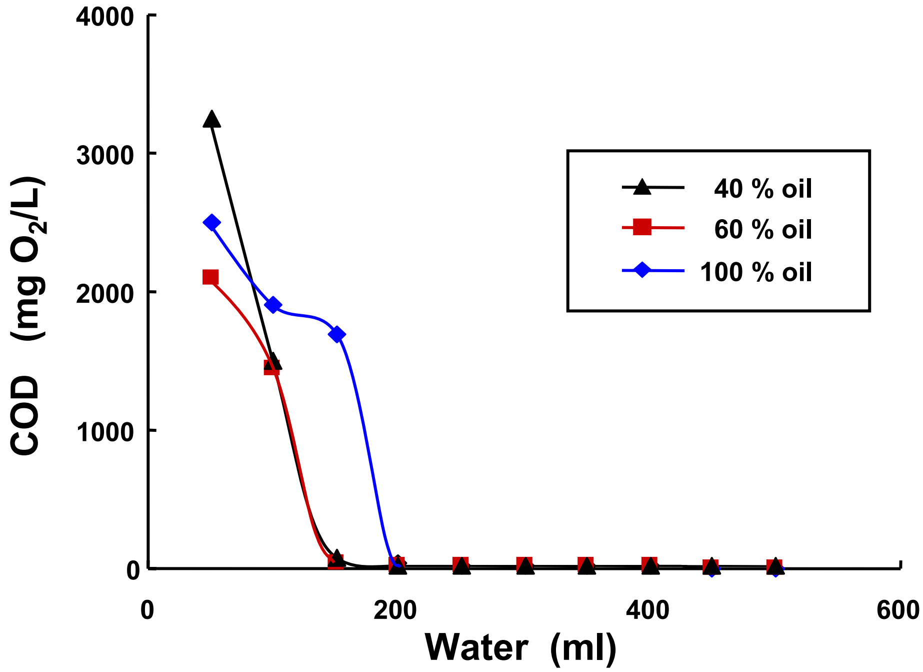

Fig. 4. Dependency of COD at different oil percentages by THL:WS (50:50) at different ratio oil:water

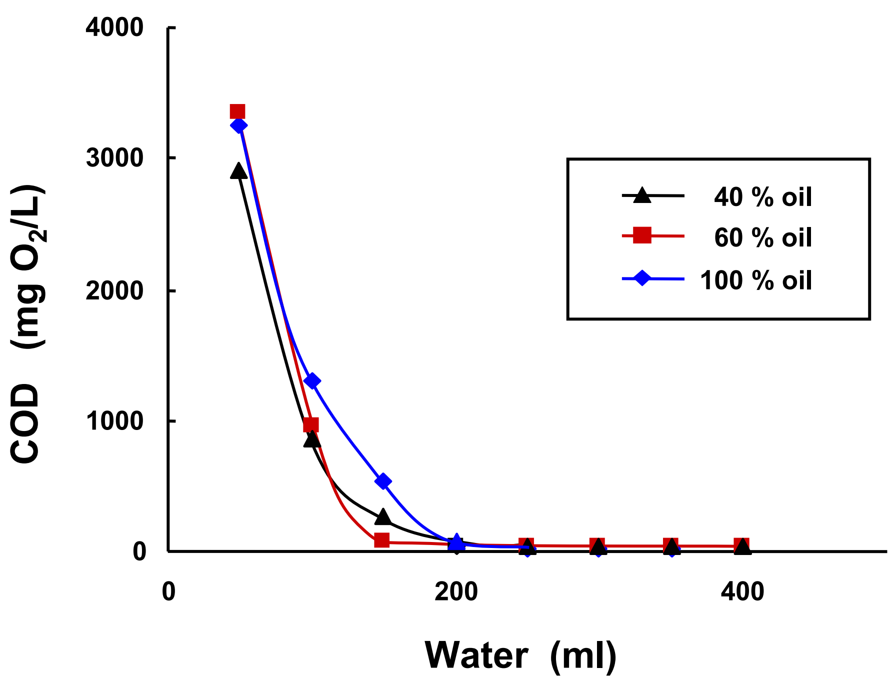

Fig. 5. Dependency of COD at different oil percentages by THL:WS (75:25) at different ratio oil:water

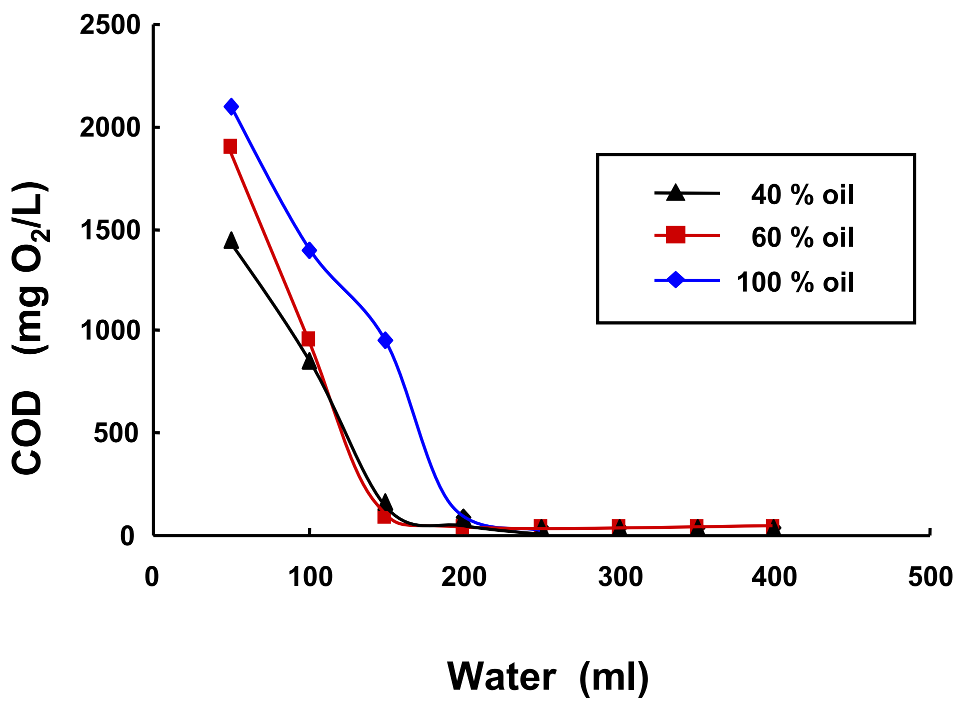

Fig. 6. Dependency of COD at different oil percentages by THL:WS (90:10) at different ratios of oil:water

The average rate of release of oil pollution from the sorbent was estimated by:

$$v_{av} = \frac{\Delta COD}{V\,\Delta\tau} \ , \qquad (1)$$

v_{av} - average rate, mg $O_2.L^{-1}.min^{-1}$;
COD - Chemical Oxygen Demand, mg $O_2.L^{-1}$;
τ - time, min;
V – volume of washing water, L.

This formula describes the COD change of polluted water for one minute. Data for the average rate of release for the three composites are shown in Figs. 7, 8 and 9.

It was established that the release of oil from THL:WS (50:50) occurred with a high rate, independently of the ratio of oil to water. However, the behavior of the curves was different. It was observed that the ratio of oil release was slowed up in the interval of 6-18 minutes at 100 % and 60 % oil. At the same time the average rate at 40 % oil was higher and the release continued uniformly. In spite of this, the composition of THL: WS (50/50) was suitable for use, because such a sorbent will retain great quantities of oil (it possesses a high sorption capacity but shows a lower release ability) (Fig.7).

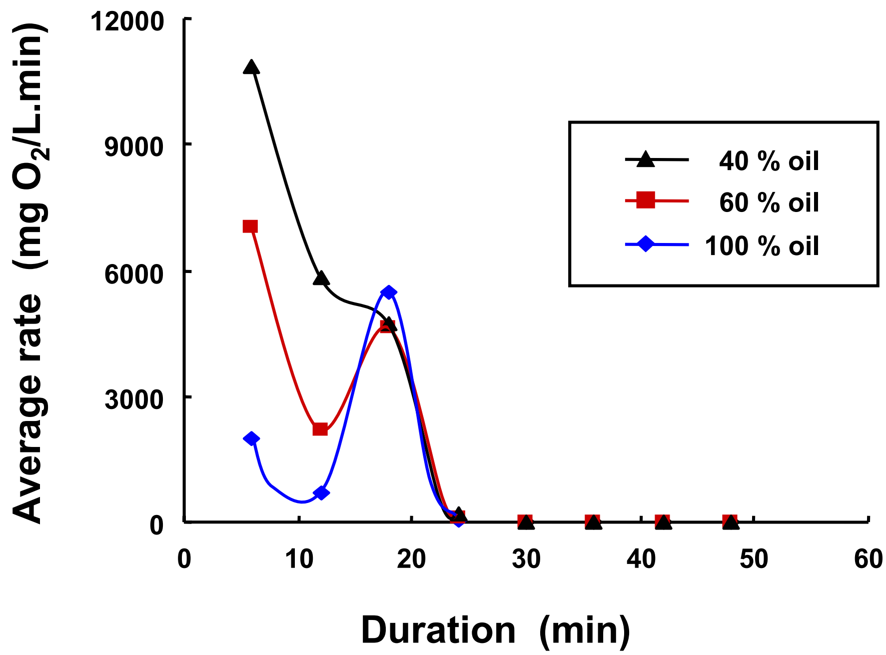

Fig. 7. Dependency of average rate of release ability at different oil percentage by THL:WS (50:50) at different ratios of oil:water

The addition of 25 % WS to THL (mixture of THL:WS equals 75/25) led to a slight increase in the average release rate in the beginning, but the initial sorption capacity of mixture was sufficiently high such that it was optimum for the sorption process. Different dependencies for the individual ratios of oil to water were observed. The rate decreased at 100 % oil in the interval up to 18 minutes. The average rate was higher at 40 % and 60 % oil (Fig. 8).

The comparison of Figs. 7, 8 and 9 shows that the average rate of release was lowest at 10 % WS in the composite. This was attributed to the good ability of THL to retain the oil, most likely due to the THL pore structure; in fact it was found that minimal release was reached at a composition of THL: WS of (90/10).

Hence, the addition of minimal WS quantities led to a decrease in the average rate of release. This fact has practical importance, because such a composite sorbent derived from THL with 10 % WS can retain the oil pollutants for a sufficiently long time to allow the oil polluted sorbent to be recycled.

CONCLUSIONS

1. The release properties of composites based on technical hydrolysis lignin (THL) with 50 %, 25 %, and 10 % wool shoddy (WS) towards oil pollution at different ratios of oil to water were studied.

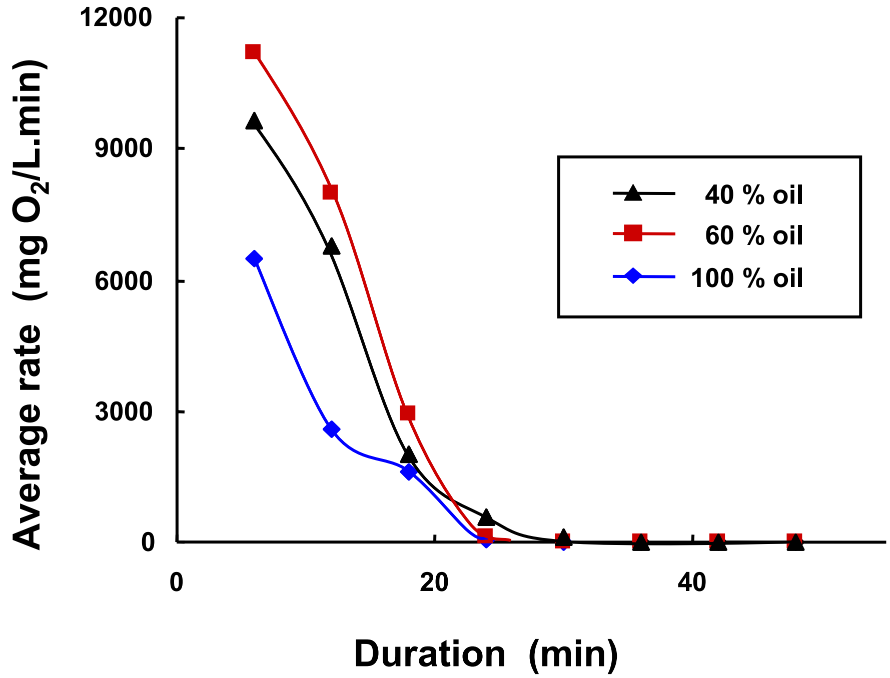

Fig. 8. Dependency of average rate of release ability at different oil percentages by THL:WS (75:25) at different ratios of oil:water

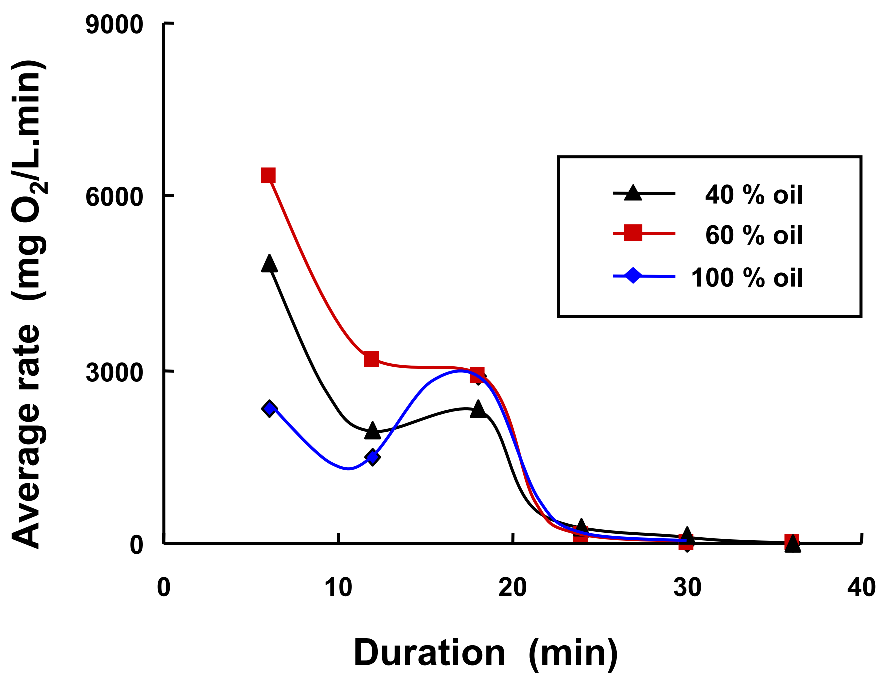

Fig. 9. Dependency of average rate of release abiity at different oil percentages by THL:WS (90:10) at different ratios of oil:water

2. It was noted that:
   - the composites were suitable for use as oil sorbents;
   - the initial sorption capacity increased considerably with an increase in the WS addition; and
   - the WS addition increased the release of oil from the composite .
3. The optimal results towards sorption and release of oil pollution were reached at a ratio of THL to WS equal to 90:10.

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REFERENCES CITED

Masahiro, O., (1994). "Optimum waste water treatment processes," *Hiomen JISSO Gijutsu* 10(4), 54.
Fletcher Ronald, D., (1994). "Practical considerations during bioremediation," *Environ.Sci*., Pollut. Control. Ser. 8, 39.
Davis, M., (1994). "Use advanced methods to treat waste water," *Hydrocarbon Process*, Int. Ed., 73(8), 43.
Chem, A., (1998). "Effect of mixing conditions on flocculation kinetics of waste water containing using fibrous materials and polyelectrolytes," *Bras. J. Chem. Eng*. 15, 358.
Eur. Pat. Appl. (1994)."Method of making sorbent articles," EP0608884.
Ronald, D., (1993). "Technical applications for wool help improve the environment," *Technical Textile International* (2), 8.
Hianov, I., (1995). "Development of sorbents from wood waste for collection of oil spills," *Forest chemistry and Org. Synthesis* 11(8), 22.
Kugin, A., (1994). "Obtaining of high effective absorbents on the basis of wood fibrous materials," *Forest chemistry and Org. Synthesis*, 10(5), 3.
Grigoriev, L., (1996). " Obtaining and application of new materials on the basis of lignin waste," *Cellulose, Paper, Cardboard* (3), 24.
Russia Patent, (1995). "Adsorbent of petroleum and petroleum products for water and soil treatment," RU2049543.
Finland Patent, (1992). "Flokkulointiaineena käyttökelpoinen kationinen ligniini ja menetelmä jätevesien puhdistamiseksi," FI912863.

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