Journal of the University of Chemical Technology and Metallurgy, 43, 2, 2008, 217-222

STUDY OF THE SORPTION PROPERTIES OF TECHNICAL HYDROLYSIS LIGNIN AND WOOL SHODDY TOWARDS OIL POLLUTION

S. Nenkova[1], M. Herzog[2], V. Gancheva[3], R. Garvanska[1]

[1] *University of Chemical Technology and Metallurgy 8 Kl. Ohridski, 1756 Sofia, Bulgaria*
[2] *University of Applied Sciences, Berlin, Wildau, Germany*
[3] *Bulgarian Academy of Science, Institute of Polymers, Sofia, Bulgaria*

Received 07 December 2007
Accepted 18 April 2008

ABSTRACT

The sorption properties of technical hydrolysis lignin (THL)and wool shoddy towards oil pollution at different concentration of contamination were studied. The release of the oil was studied by weight method as well as by determining COD of the treated water. It has been established that THL possesses low ability release back to the water and low rate of reaching the equilibrium but wood shoddy possess higher ability and higher rate for reaching of the equilibrium.

Keywords: technical hydrolysis lignin, wool shoddy, sorbents, oil pollution, equilibrium.

INTRODUCTION

Oil spills that occur from river-going vessels, in ports, and from manufacturing facilities adjacent to rivers are an exceptionally serious 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 location of the pollution.

A number of papers [1-3] are related to using biological processes for water treatment, but these methods are not applicable for the typical situations. In those cases the usage of highly effective fibrous-polymer sorbents may be of importance.

Papers and patents on highly fibrillated fibrous materials for cleaning failing protein water [4], micro fibrous sorbents on the basis of thermoplastic polymers [5], wool fibrous materials of high surface area for cleaning of oil floods in Persian Gulf in 1990 are available [6]. Testing of wood saw dusts for the cleaning of water surface from average oil floods [7], preparation of highly effective sorbents on the basis of fibrous waste from paper production [8] and the use of lignin containing waste for cleaning water [9,10] have also been reported.

The possibilities for overcoming restricting 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 and waste products with high sorption ability. Of special interest in this respect are the wool shoddy (WS) and the technical hydrolysis lignin (THL). They possess highly developed surface, 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 [11].

The sorption of the lignin under dynamic turbulent conditions has been investigated. The increasing of the turbulation leads to a higher sorption extent. The extent of sorption depends on the ratio of oil product to lignin. Two technological schemes for the remediation of oil polluted water with hydrolysis lignin have been developed [12].

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., they must possess a low desorption rate.

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

The aim of the present investigation is to provide a study on the desorption characteristics of technical hydrolysis lignin and wool shoddy related to oil polltants at different contaminant concentrations.

EXPERIMENTAL

Materials

The whole work has been conducted with the following materials:

- technical hydrolysis lignin (THL), obtained by acid hydrolysis of wood in industry deposited in 2001 near the town Razlog, Bulgaria; fraction 0,125-0,315 mm.
- wool shoddy (WS) consisting of 50 $\%_{mass}$ wool, 25 $\%_{mass}$ viscose, and 25 $\%_{mass}$ polyamide)

A crude oil with 0,85 g/cm^3 specific weight and pH 7 is used for oil pollution oil/water ratios 10:0 (100 $\%_{mass}$ oil); 6:4 (60 $\%_{mass}$ oil) and 4:6 (40 $\%_{mass}$ oil).

Techniques

Two methods to study the release characteristics have been used.

Weight method for the determination of the oil flow. The desorption properties were investigated at constant temperature (20^{o}C). A glass tube with diameter d=25 cm and height h=55cm was used. Material: THL or WS were put in the tube after that the oil or the mixture of oil/water was poured on. The oil released quantity was measured during a period of 270 min at regular intervals after a 15 min wait time for obtaining the maximum sorption of oil pollution.

The release of the bound oil was accomplished by measuring Chemical Oxygen Demand (COD). 50 ml water was poured into the THL or WS that were in the glass tube after completion of desorption process by the weight method. After a period of 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 oil containing fractions was then determined.

RESULTS AND DISCUSSION

The experimental data on the release of the oil pollutants from THL and WS at the three ratios of oil/water, are shown in Fig.1 and Fig. 2.

It can be seen from Fig.1 that the release at 100 % oil pollution is steady and quick up to 17 minutes, afterwards a certain retention follows and a further slow release up to 270 minutes is observed.

At the ratios 6:4 and 4:6 oil/water initially a release only of water, contained in the mixture, is observed. This is due to the higher adhesion of THL and the oil. At the ratio 6:4 this process continues 3 minutes, and at 4:6 – 7 minutes. The reason for this is the higher water quantity at this ratio. After this period the desorption is slow and uniform up to 60 minutes at 6:4 and up to 270 minutes at 4:6 ratio. Therefore, release equilibrium is reached more quickly at the higher oil

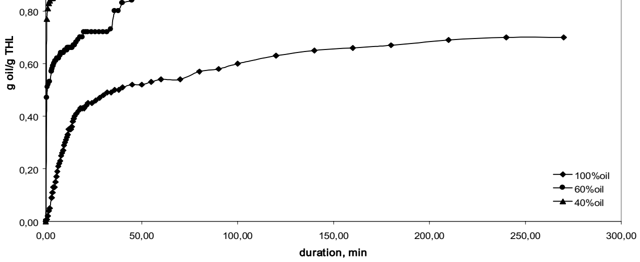

Fig. 1. Released quantity of oil by THL at different percentages of oil.

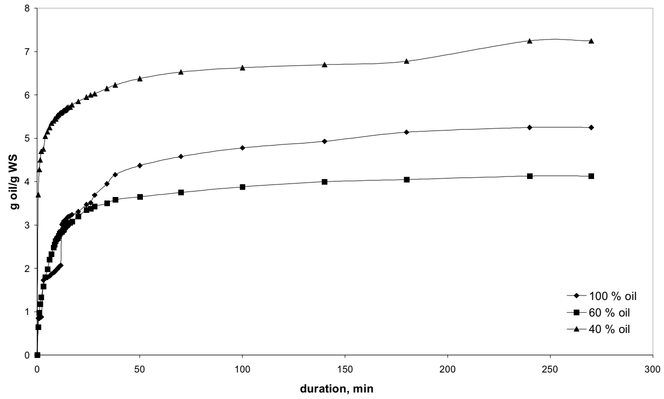

Fig. 2. Released quantity of oil by WS at different percentages of oil.

content. The value of the oil released quantity at the three ratios is similar.

It can be seen from Fig. 2 that the release at 100 % (10:0) oil pollutant concentration from WS is rapid and the release equilibrium is reached after 14 minutes. At the ratio 6:4 the dependence is similar but at ratio 4:6 the release is longer – 270 minutes. Initially a release only of water, contained in WS is not observed.

The established dependences are confirmed as well by the oil retained quantities (g oil/g THL and WS) at ratio oil/water: 10:0; 6:4; 4:6 (Table 1).

The data for COD, characterising persorption (the sorption in pours of materials), at the three ratios of oil/water- 10:0; 6:4; 4:6 are presented in Fig. 3 for THL and Fig. 4 for WS.

The dependences are like those for the physical desorption, determined by the weight method.

The average rate of release ability 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 persorption and partially by physical absorption, is separated.

The contamination of this released water was determined by COD. The average rate of release of oil pollution from sorbent is estimated by the formula:

$$v_{av} = \frac{\Delta COD}{V \, \Delta\tau},$$

v_{av} - average rate, mg O_2 dm^{-3} min^{-1};
COD - Chemical Oxygen Demand, mg O_2 dm^{-3};
τ - time, min;
V – volume of the washing water, dm^{-3}.

This formula describes the COD change of polluted water for one minute.

The data for the average rate of release for THL and WS are shown in Figs. 5 and 6. It was established (Fig. 5) that oil particles are retained very well by THL independently from the ratio of oil/ water due to pore structure of the material.

At WS the release of oil pollution is quick (Fig. 6) independently by of the ratio of oil: water. WS has high sorption ability, as well as high rate of release of oil pollutants.

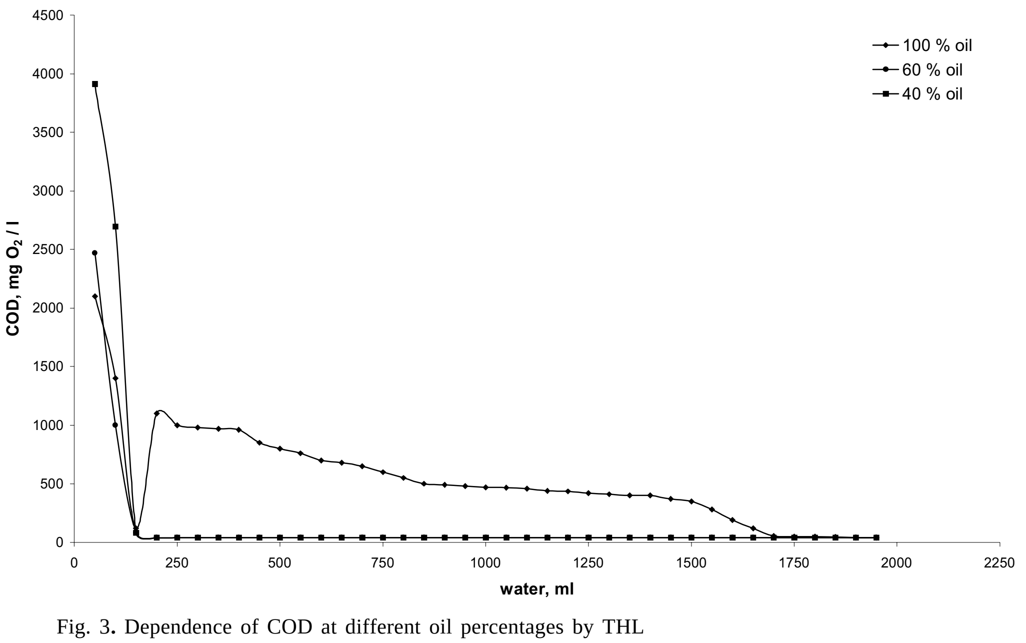

Fig. 3. Dependence of COD at different oil percentages by THL

Table 1. Oil retained quantity g oil/g THL and WS.

Duration, min	THL			WS		
	100% oil	60% oil	40% oil	100% oil	60% oil	40% oil
0	2,87	3,05	3,28	10,75	11,43	12,29
0,5	2,86	2,58	2,51	9,90	10,78	8,59
1	2,84	2,54	2,47	9,87	10,45	8,01
1,5	2,82	2,53	2,45	9,87	10,25	7,79
2	2,81	2,52	2,44	9,87	10,10	7,59
3	2,78	2,48	2,43	7,90	9,85	7,34
4	2,74	2,46	2,42	7,13	9,63	7,24
5	2,71	2,44	2,41	6,45	9,45	7,14
6	2,67	2,43	2,41	5,85	9,23	7,04
7	2,65	2,43	2,40	5,78	9,10	6,94
8	2,61	2,41	2,40	5,78	8,95	6,89
8,5	2,60	2,41	2,39	5,75	8,88	6,84
9	2,59	2,41	2,39	5,75	8,80	6,84
9,5	2,58	2,41	2,39	5,68	8,75	6,79
10	2,57	2,40	2,39	5,68	8,73	6,76
10,5	2,56	2,40	2,38	5,65	8,68	6,74
11	2,55	2,40	2,37	5,65	8,63	6,71
11,5	2,53	2,39	2,36	5,65	8,60	6,70
12	2,52	2,39	2,36	5,63	8,58	6,69
12,5	2,52	2,39	2,35	5,63	8,53	6,66
13	2,52	2,39	2,34	5,63	8,48	6,65
13,5	2,51	2,39	2,34	5,50	8,45	6,64
14	2,49	2,39	2,33	5,50	8,43	6,62
14,5	2,48	2,38	2,33	5,50	8,40	6,59
15	2,47	2,38	2,33	5,50	8,38	6,57
16	2,46	2,37	2,32	5,50	8,35	6,54
17	2,45	2,36	2,32	5,50	8,33	6,52
20	2,44	2,33	2,30	5,50	8,18	6,44
24	2,42	2,35	2,29	5,50	8,05	6,34
26	2,41	2,33	2,28	5,50	8,00	6,29
28	2,40	2,33	2,28	5,50	7,98	6,26
34	2,38	2,32	2,25	5,50	7,90	6,14
38	2,37	2,25	2,24	5,50	7,83	6,06
50	2,35	2,19	2,21	5,50	7,75	5,91
70	2,33	2,14	2,19	5,50	7,63	5,76
100	2,27	2,14	2,16	5,50	7,50	5,66
140	2,22	2,14	2,15	5,50	7,40	5,59
180	2,20	2,14	2,15	5,50	7,35	5,51
240	2,17	2,14	2,15	5,50	7,30	5,04
270	2,17	2,14	2,15	5,50	7,30	5,04

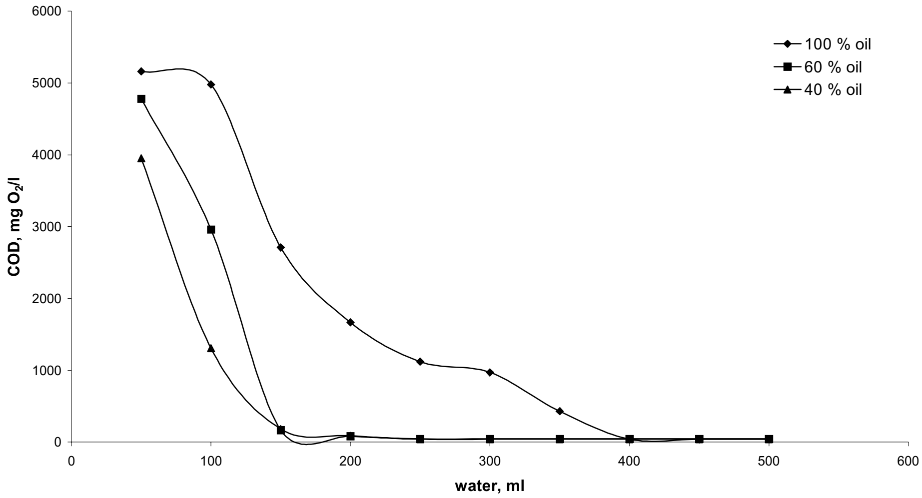

Fig. 4. Dependence of COD at different oil percentages by WS.

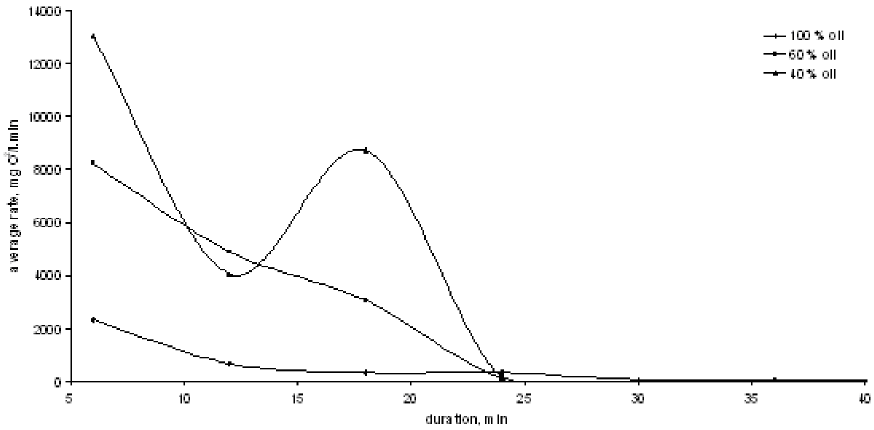

Fig. 5. Dependence of average rate of release ability by THL of different oil percentages.

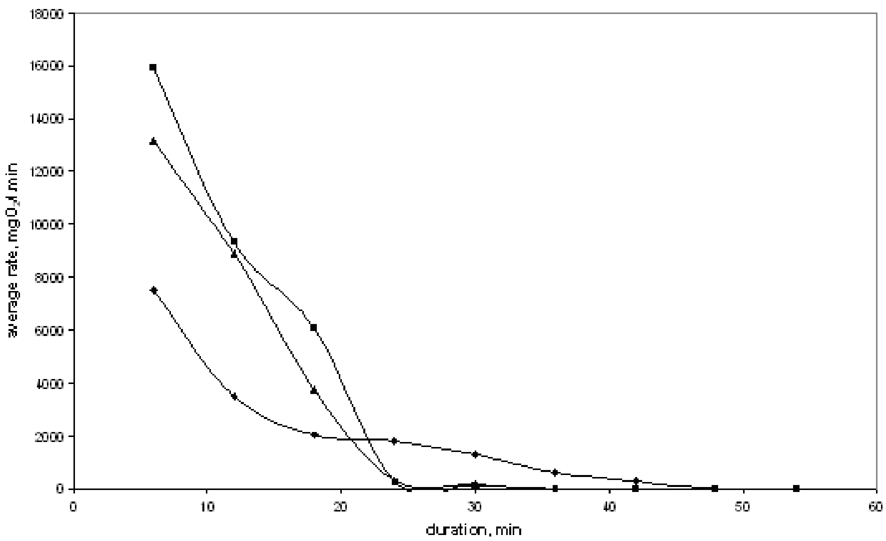

Fig. 6. Dependence of average rate of release ability by WS of different oil percentages.

CONCLUSIONS

The release properties of THL and WS towards oil pollution at different ratios of oil: water were studied.

It is worth mentioning that technical hydrolysis lignin possesses comparatively good initial sorption capacity, low release ability of oil pollution and low rate of reaching release equilibrium.

In contrast to THL, WS possess very high initial sorption capacity but high release ability of oil pollution and high rate of reaching release equilibrium.

Therefore, the established dependences show that mixtures of THL and WS will be very suitable for preparing sorbents for cleaning of oil polluted waters.

Acnowledgements

The authors are grateful for the support of NATO on Collaborative Linkage Grand- Ref. 982877 "New Technologies for oil pollution clean-up".

REFERENCES

1. O. Masahiro, Hiomen JISSO Gijutsu,10,4,1994,54.
2. D. Ronald, Environ.Sci., Pollut. Control, Ser.8, 1994, 39.
3. M.Davis, Hydrocarbon Process., 73 ,8, 1994, 43.
4. A.Chem, Bras. J. Chem. Eng.,15, 1998, 358.
5. Eur. Pat. Appl. EP 608, 884.
6. D. Ronald, Technical Textile International, Ser.2, 1993, 8.
7. I.Hianov, Forest chemistry and Org. Synthesis, 11, 8, 1995, 22.
8. A.Kugin, Forest chemistry and Org. Synthesis, 10,5, 1994, 3.
9. L.Grigoriev, Cellulose, Paper, Cardboard, 3, 1996, 24.
10. B. Koumanova, S. Nenkova, K. Stanulov, Cost-effective Adsorbents for Removal of Crude Oil and Hydrocarbons from Polluted Waters, 1st Int. Congress on Petroleum Contiminated Soils, Sediments & Water, August 14-17, 2001, Imperial College, London, UK.
11. Russia Patent, 2001, N 20 495 43.
12. Finland Patent, 1984, N 91 642.