Environment Protection Engineering

Vol. 9 1983 No. 1

JANUSZ RYBKA*

COALESCENCE OF EMULSIFIED OILY WASTEWATER BY POLYURETHANE FOAM BEDS

The problems of oil–water emulsion breaking are presented. Oil contained in industrial wastewater is removed by coalescence on polyurethane beds. Some of the parameters of the coalescence process, the coalescer properties, and the efficiency of oil removal from industrial wastewater are discussed in detail. For the mechanically stabilized oil–water emulsions an oil removal of 98% to 99.5% is achieved. Oil concentration in the effluent from the coalescence bed is as low as 5–10 ppm.

The experimental results, as well as the physicochemical properties of polyurethane in general, and its oil-absorption capacity in particular, substantiate the application of polyurethane foam beds to the treatment of emulsified oily wastewater. The use of polyurethane beds is both highly efficient and highly promising for future applications.

1. INTRODUCTION

The commercial importance of polyurethanes dates back to the nineteen sixties and specifically to the period from 1962 to 1966 [11]. Since then, the application range of these materials has continued to increase throughout the world, and substantial advances are reported in the technology of foamed polyurethanes [16].

The physicochemical properties of polyurethane foams in general, and their oil-asborption capacity in particular, along with the easiness of their regeneration, support the applications of these sorbents in stream pollution control [1, 3–5, 7, 9, 12, 13, 18, 20]. Foamed polyurethanes can be used for oil removal from water as buoyancy [21, 22], as the belts in a closed system [14, 23, 24], as sorbing elements working in an oil separator [25, 26] or as a sorbent for oil-spill recovery [19]. Porous polyurethane foam can also be applied in the filtration of industrial wastewater for oil removal [10] or coalescence of emulsified oily wastewater [15, 27, 28]. The most promising property of foamed polyurethanes is their ability to retain suspended solids on the entire surface area, thus extending the length of

---

* Institute of Environment Engineering, Technical University of Łódź, 93-590 Łódź, al. Politechniki 6, Poland.

the filter bed performance and decreasing head loss [17]. Another favourable advantage of polyurethane foams is their mechanical strength and chemical resistance. The experimental results for elastic porous foam polyurethanes indicate that their applications in stream pollution control will continue to increase.

In this paper, the usability of domestic polyurethane foams in the filtration process for coalescence of oil emulsions is studied.

2. EXPERIMENTAL

2.1. APPARATUS

The coalescence of oil–water emulsions (referred to as O/W emulsions) on polyurethane beds was studied in the system shown in fig. 1 [8]. Tap water entering the manostat (*1*) is sent to a thermostat (*2*) to be heated up to a temperature of 293 K. From there, it passes

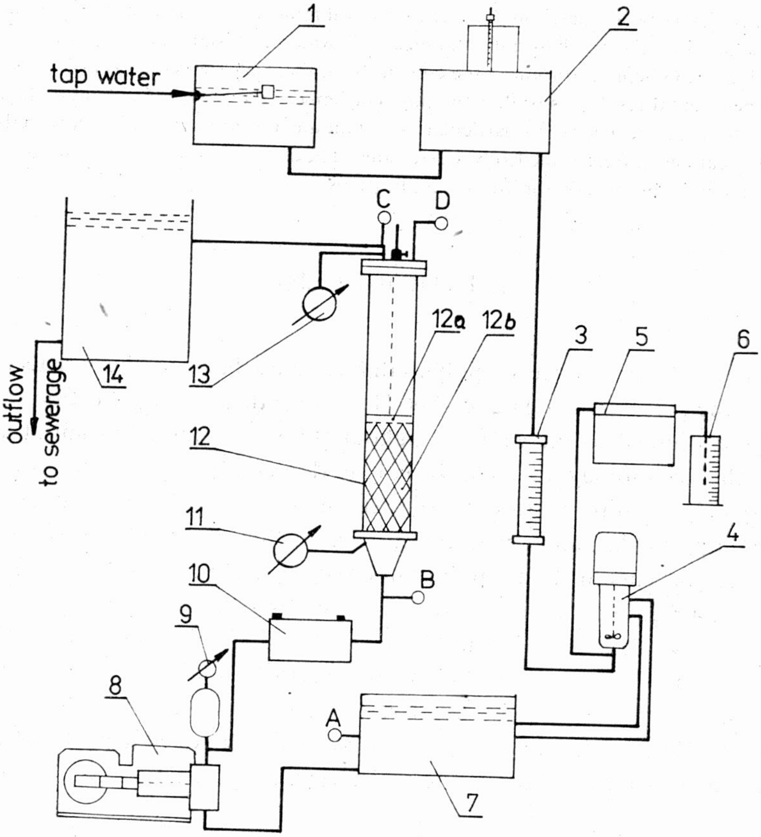

Fig. 1. Experimental apparatus

Rys. 1. Aparatura doświadczalna

(by gravity) through a rotameter (*3*) to enter a homogenizer (*4*). Lux 8 oil, contained in tank (*6*), is supplied to the homogenizer (*4*) by means of a dosing pump (*5*). The O/W emulsion is passed (by gravity) to a separator (*7*) in which it is retained for 10 minutes. Thus, larger droplets are removed. To measure the oil content, samples are collected at point *A*. A piston pump (*8*) of a constant throughput transports the emulsion from the separator (*7*) through a tank (*10*) to a coalescence filter (*12*). The pressure of the passing medium is measured with a manometer (*9*). Before entering the coalescence filter (*12*), the medium is subject to deaeration, stabilization and separation which take place in tank (*10*). The emulsion entering the coalescence filter is sampled at point *B*, and its pressure is monitored by a manometer (*11*). The coalescence filter is made of a plexiglass pipe having an internal diameter of 0.060 m and a cross-section of 28.26×10^{-4} m^2. At each end of the pipe a dismantleable flange has been attached. The outlet flange is combined with a manometer (*11*). The coalescer bed (*12 b*) is supported by a sieve. In the top flange, there is an outlet pipe (*D*) for the oil leaving the column after the coalescence process has been completed, and another pipe for water outflow. In the latter, a sampling outlet (*C*) and a manometer (*13*) are installed. From the indications by manometers (*11*) and (*13*) the head loss throughout the filter bed can be determined. A perforated piston (*12 a*) is placed inside the pipe to support and regenerate the foam polyurethane filter bed, as well as to control the packing density. The O/W emulsion passes through the coalescer from bottom to its top. Water separated in the coalescence process enters a tank (*14*) which can be used for pump throughput control and also as a separator. The effluent water is sent to the sewerage system.

2.2. SELECTION AND PREPARATION OF EXPERIMENTAL MATERIAL

The separation efficiency of the coalescence filter depends on the properties of the material used [2, 6]. The basic requirement for a coalescer is its affinity to oil, i.e. oleophily. The affinity of polyurethane foams to the oil is influenced by the internal structure of the material and by the components used for their preparation [9].

Both oleophily and hydrophily were determined by the "sitting droplet" method. The determinations involved commercial polyurethane foams manufactured by Polish firms and polyurethane foam mouldings prepared by the author of this report.

Oleophily was established in terms of the wetting angle of Lux 8 oil having a density of 884 kg/m^3 and a viscosity of 216 cP. Hydrophily was expressed in terms of the wetting angle of tap water. Table 1 lists measured wetting angles of the two liquids employed in this study. As shown in this table, polyurethane foams are both oleo- and hydrophilous because the wetting angle of water is less than 90 deg. Oleophily decreases with the increasing density of the foams. The data for Samples I through III indicate that there is a possibility of manufacturing coalescers with good oleophilous properties. Of the foams listed in tab. 1, the polyether T-25 type foam is best suited for our purpose because of the relatively low cost of its manufacturing. T-25 foams are also readily available on the Polish market. The T-25 polyether foams involved in the experiments had an apparent density of 25 kg/m^3 and

Table 1

Oleophily and hydrophily of domestic foamed polyurethanes
Oleofilność i hydrofilność piankowych poliuretanów krajowych

Type and symbol of foam	Wetting angles for Lux 8 oil	Wetting angles for water
T-25 Polyether	42°	60°
T-31 Polyether	45°	62°
T-42 Polyether	53°	70°
S-28 Polyester	32°	65°
S-URL-75 Polyester	37°	70°
Sample I Polyether	5°	60°
Sample II Polyester	5°	100°
Sample III Polyester	16°	78°

a linear density of about 20 pores/cm. T-42 polyether foams were tested as a reference system.

The preparation of the elastic polyurethane foam coalescer consisted of the following steps: stamping of 0.064 m diameter and 0.022 m thick disks, drying at 353 K, weighing and placing the disks in the coalescer. The density of the packing was determined with the use of a piston.

2.3. O/W EMULSIONS

Tap water of a temperature of 293 K was passed to the homogenizer at a rate of 120×10^{-3} m^3/h. Lux 8 oil in a given amount was dosed to the homogenizer which was set in motion. The mixing rate was kept constant. Two sets of O/W emulsions were prepared. Their stability was determined by retention in the separators. Oil content versus time of separation is plotted in fig. 2.

2.4. EXPERIMENTAL PROCEDURE

Considering the complex nature of the coalescence process [2, 6], the experiments were carried out with variable parameters of the filter bed and with the O/W emulsion described above. The flow rate of the medium was constant throughout the experiments and equal to 0.050 m^3/h to give a hydraulic loading of the filter of 17.69 $m^3/m^2/h$.

The coalescence process was carried on until a rapid increase of oil content in the effluent from the filter bed was observed. After 60 seconds, the measured medium was extracted with the use of CCl_4. Oil was analyzed by fluorometry.

The filter bed was regenerated mechanically by compressing the polyurethane foams in a press. The amounts of oil both squeezed out and remaining in the foamed polyurethanes were measured.

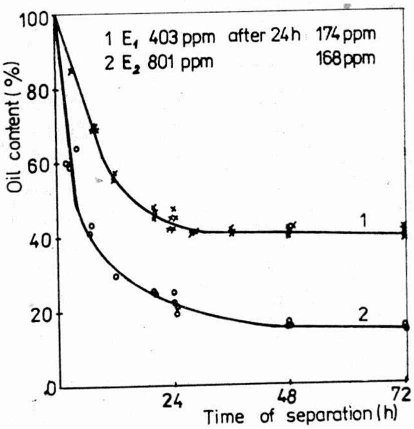

Fig. 2. Oil content in water versus time of separation

Rys. 2. Zawartość oleju w wodzie w zależności od czasu rozdzielania

3. RESULTS AND DISCUSSION

Table 2 gives the parameters for each of the experimental runs and the efficiencies of oil removals. The O/W emulsions shown in fig. 2 differed from one another in initial concentration of oil. When the time of separation was equal to or longer than 24 h the differences in oil content between the two sets of O/W emulsions were insignificant (after 24 h, $E_1 = 174$ ppm, and $E_2 = 168$ ppm). Thus, it was anticipated that their stabilities were similar, the more so as the times of complete separation were almost the same.

Oil removal efficiencies obtained on the experimental beds (having a packing of 58 kg/m^3) are plotted in fig. 3. As shown by these plots, the efficiency of the coalescence filter was unstable, being manifested by the rapid changes of oil content in the effluent. This can be attributed to the self-compressing of the coalescer during filter run. The increment of pressure loss in the bed (resulting from the saturation with oil) brings about a decrease in the volume of the polyurethane foams. Thus, 0.34 m and 0.33 m high coalescer beds showed packing densities equal to or higher than 116 kg/m^3 in the last phase of the experimental run. The rapid increase in pressure loss is shown in fig. 4.

Figure 5 characterizes the performance of a coalescence filter with a packing of 116 kg/m^3. The packing was used one, two or three times after mechanical regeneration by compressing. The effectiveness of such a filter is more stable than that of a filter with a 0.058 kg/m^3 packing. The changes observed in the bed volume are insignificant. The former filters took a shorter time to reach the state of saturation, thereupon the pressure loss in the coalescers began to increase rapidly (fig. 6).

Table 2

Experimental parameters

Parametry doświadczenia

Run No.	Type of polyurethane foam	Emulsion	Weight of bed kg	Packing density kg/m³	Bed depth m	Multiplication factor of foam reduction	Oil content in the effluent ppm	Removal efficiency %
1	T 25	E_1*	0.016246	58	0.10	2.3	53.0	87
2	T 25	E_1	0.016336	116.0	0.05	4.6	46.0	89
3	T 25	E_1	0.032721	58	0.20	2.3	33.0	92
4	T 25	E_1	0.032794	116	0.10	4.6	27.0	93
5	T 25	E_1	0.032765	230	0.05	9.2	24.0	94
6	T 25	E_2**	0.054554	230	0.085	9.2	3.5	99.6
7	T 25	E_2	0.055786	116	0.17	4.6	5.0	99.4
8	T 25	E_2	0.055728	58	0.34	2.3	4.0	99.5
9	T 25	E_2	0.072115	116	0.22	4.6	3.0	99.6
10	T 25	E_2	0.072019	58	0.44	2.3	3.0	99.6
11	T 42	E_2	0.071215	84	0.30	2.0	15.0	98.0
12	T 42	E_2	0.113934	84	0.48	2.0	6.0	99.3
13	T 25	E_1	0.032794***	116	0.10	4.6	21.0	95
14	T 25	E_2	0.055786***	116	0.17	4.6	4.0	99.5
15	T 25	E_2	0.072115***	116	0.22	4.6	1.5	99.8
16	T 25	E_2	0.072115****	116	0.22	4.6	2.5	99.7
17	T 42	E_2	0.081887***	97	0.30	2.3	4.0	99.5

* $E_1 = 403$ ppm.
** $E_2 = 801$ ppm.
*** Reused bed.
**** Saturated bed.

From fig. 7 it is seen that the run of a bed with a 230 kg/m³ packing is quite short, and the resulting pressure losses are considerable (fig. 8).

Satisfactory removal of oil, when the oil content in the effluent was less than 10 ppm, was obtained for a weighed coalescer sample of 0.055 kg at packings of 116 kg/m³, 58 kg/m³, and 230 kg/m³ at the respective bed depths of 0.17 m, 0.34 m, and 0.085 m. Oil removals achieved under these conditions varied from 99.4% to 99.5%, and for a weighed 0.072 kg sample being equal even to 99.8%.

As shown in figs. 3, 5, 7 and in tab. 2, oil removals on polyurethane foam beds of a small depth are packing-dependent. When the bed depth was increased, the density of the packing (i.e. the decrease in the initial volume of the foams) did not influence the efficiency of oil removal.

There is, however, a strong relationship between the run duration and packing volume. The length of run duration for a filter with a 230 kg/m³ packing was found to be especially

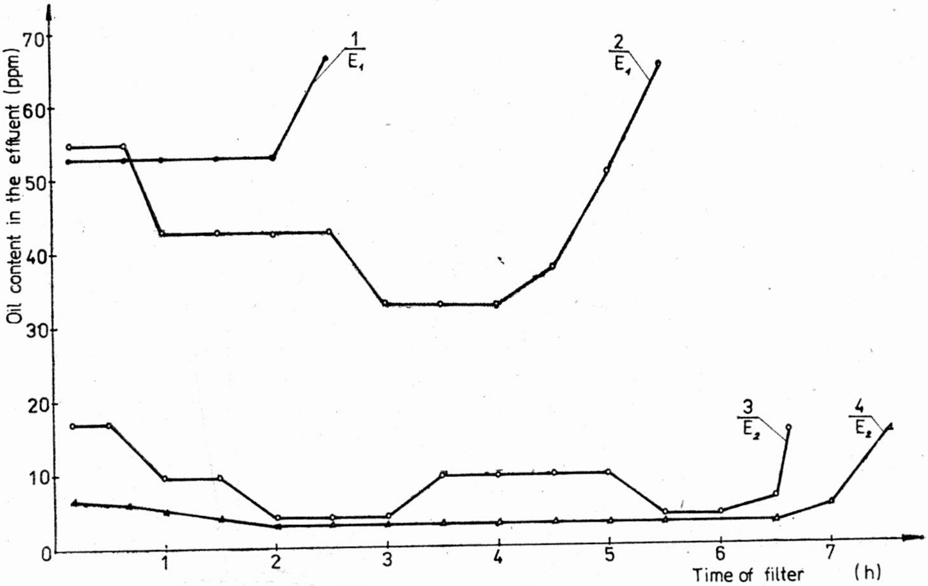

Fig. 3. Oil removal efficiency of polyurethane foam beds

1 — run 1, *2* — run 3, *3* — run 8, *4* — run 10

Rys. 3. Efektywność usuwania oleju przez piankowe złoża poliuretanowe

1 — doświadczenie 1, *2* — doświadczenie 3, *3* — doświadczenie 8, *4* — doświadczenie 10

short. The longest duration of runs were measured for a 58 kg/m^3 bed packing. The difference in the duration lengths of the runs decreased with the increasing bed depth.

The pressure losses observed at the beginning of the process did not change substantially with the change in the packing density. As the saturation with oil in the filter bed increased, so did the pressure loss. The latter was especially rapid for a packing density of 116 kg/m^3 and 230 kg/m^3.

Table 3 shows some of the results for a regenerated bed (after mechanical compressing), i.e. the quantities of squeezed out oils and those retained in the polyurethane foams. It should be noted here that after successive regeneration procedures the quantity of oil retained in the foams continued to increase. This increment can be reduced by repeated compressing in an aqueous medium. Polyurethane foams which had been subject to mechanical regeneration showed the same ability to remove oils as before, and they brought about a certain decrease in the lenght of the filter cycle duration (fig. 5, tab. 2).

The 17.69 m/h rate of emulsion flow through the filter employed in the experiments at the saturation levels given in tab. 3 accounted for very high internal velocities in the coalescer. At these saturation levels the effluent contained not only large oil drops, but also very small droplets of about 100 to 200 μm, which had not been separated in the upper part of the filter. They entered the effluent and contributed to a rapid increase in the oil content. The application of a separator allowed their separation from water, thus contributing to

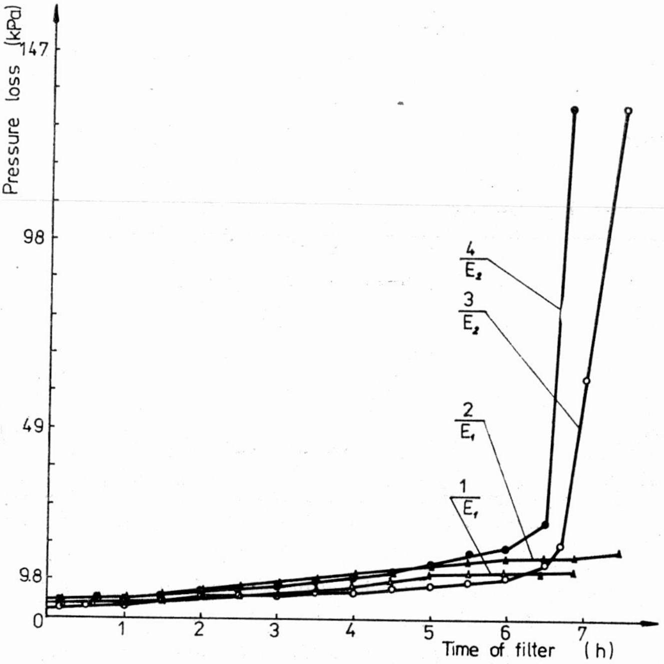

Fig. 4. Pressure loss in the course of the process

For explanations see fig. 3

Rys. 4. Spadek ciśnienia w trakcie procesu

Objaśnienia jak na rys. 3

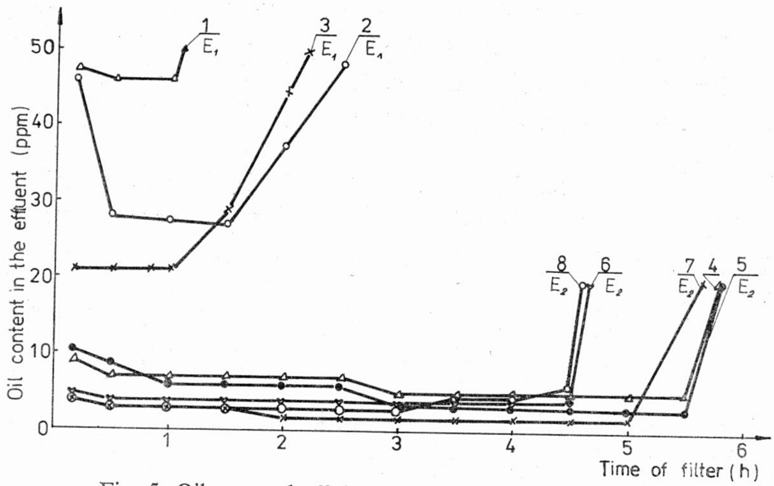

Fig. 5. Oil removal efficiency of polyurethane foam beds

1 — run 2, *2* — run 4, *3* — run 13, *4* — run 7, *5* — run 9, *6* — run 14, *7* — run 15, *8* — run 16

Rys. 5. Efektywność usuwania oleju przez piankowe złoża poliuretanowe

1 — doświadczenie 2, *2* — doświadczenie 4, *3* — doświadczenie 13, *4* — doświadczenie 7, *5* — doświadczenie 9, *6* — doświadczenie 14, *7* — doświadczenie 15, *8* — doświadczenie 16

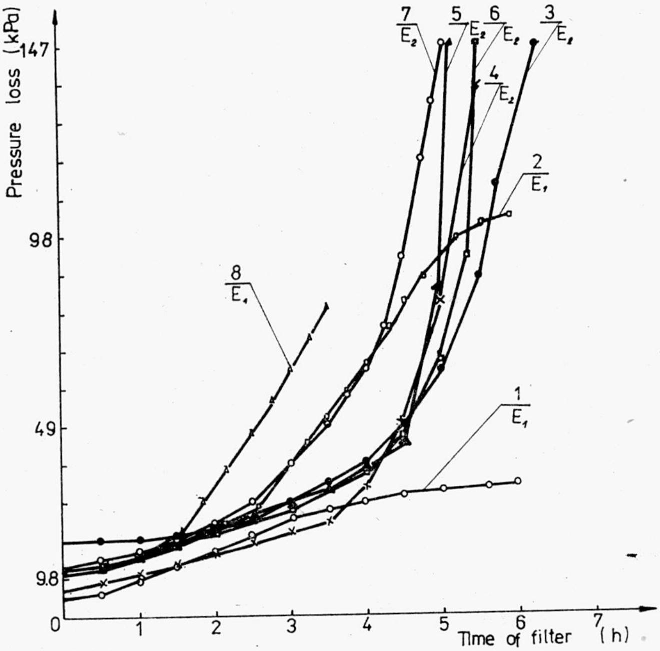

Fig. 6. Pressure loss in the course of the process

1 – run 2, *2* – run 4, *3* – run 7, *4* – run 14, *5* – run 9, *6* – run 15, *7* – run 16, *8* – run 13

Rys. 6. Spadek ciśnienia w trakcie procesu

1 – doświadczenie 2, *2* – doświadczenie 4, *3* – doświadczenie 7, *4* – doświadczenie 14, *5* – doświadczenie 9, *6* – doświadczenie 15, *7* – doświadczenie 16, *8* – doświadczenie 13

Table 3

Results of coalescer regeneration

Wyniki regeneracji koalescera

Run No.	Oil squeezed out of the bed during regeneration ml	Oil persisting in the bed ml	Total amount of oil saturating the bed ml	Oil persisting in the bed (related to bed volume) %	Oil saturating the bed (related to bed volume) %
6	15	23.2	38.2	9.65	15.9
8	86	38.7	124.7	4.10	11.8
9	86.5	30.6	117.1	5.0	19.0
10*	98	31.5	129.5	2.70	11.0
12	16.5	16	32.5	1.4	2.4
14	68	47.5	115.5	10.1	24.6
15	76.5	57.8	134.3	9.4	21.9
16	123.5	80.63	204.1	13.3	33.6
17	39.0	54.0	93.0	6.4	11.0

* Volume of the bed was decreased in the course of the filter cycle.

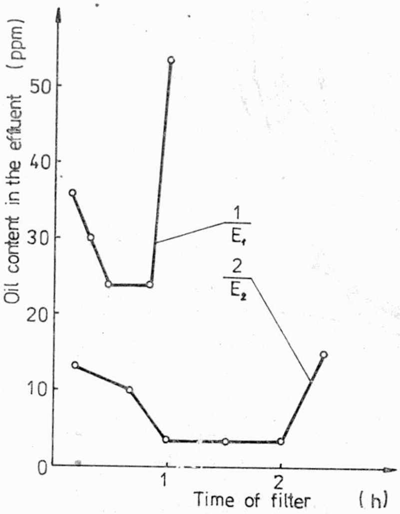

Fig. 7. Oil removal efficiency of polyurethane foam beds

1 — run 5, *2* — run 6

Rys. 7. Efektywność usuwania oleju przez piankowe złoża poliuretanowe

1 — doświadczenie 5, *2* — doświadczenie 6

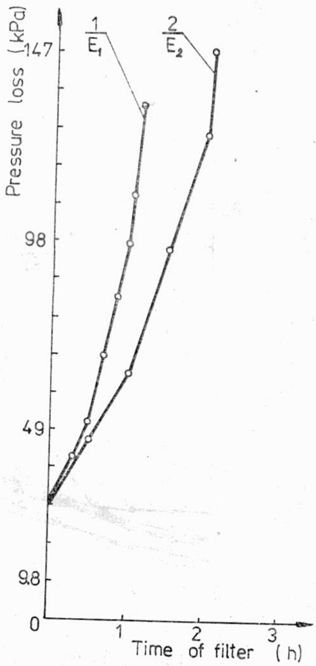

Fig. 8. Pressure loss in the course of the process

For explanations see fig. 7

Rys. 8. Spadek ciśnienia w trakcie procesu

Objaśnienia jak na rys. 7

the increase of the coalescence filter performance, which can be assumed higher than it is seen from the curves in figs. 3 through 8 (for low bed depths).

The experimental results obtained for T-42 foams which are characterized by a low oleophily and hydrophily are shown in figs. 9 and 10. Coalescence beds made of that kind of foams have a substantial influence on the filter cycle duration which is very short and is associated with a rapidly increasing pressure loss. Oil contents in the effluents from both T-42 and T-25 filter beds were compared and the results are listed in tab. 2. It is worth noting that, after the break of the filter cycle, T-42 foams exhibit lower saturation levels than to T-25 foams (tab. 3). Regenerated T-42 foams are characterized by longer working cycles.

4. CONCLUSIONS

1. Commercial foamed polyurethanes which being marketed in Poland are a good packing material that can be used in coalescence filters for O/W emulsion breaking.
2. Of the polyurethane foams tested, T-25 foams are best suited to be used as coalescers because of the low cost of manufacture and availability on the Polish market.

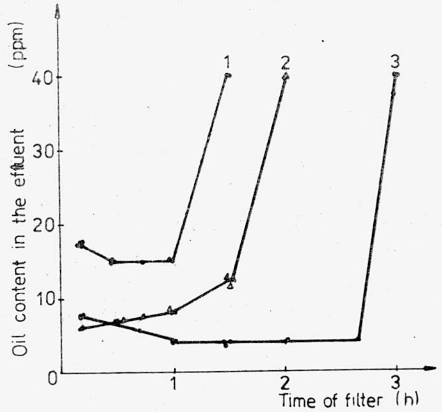

Fig. 9. Oil removal efficiency of polyurethane foam beds

1 – run 11, *2* – run 12, *3* – run 17

Rys. 9. Efektywność usuwania oleju przez piankowe złoża poliuretanowe

1 – doświadczenie 11, *2* – doświadczenie 12, *3* – doświadczenie 17

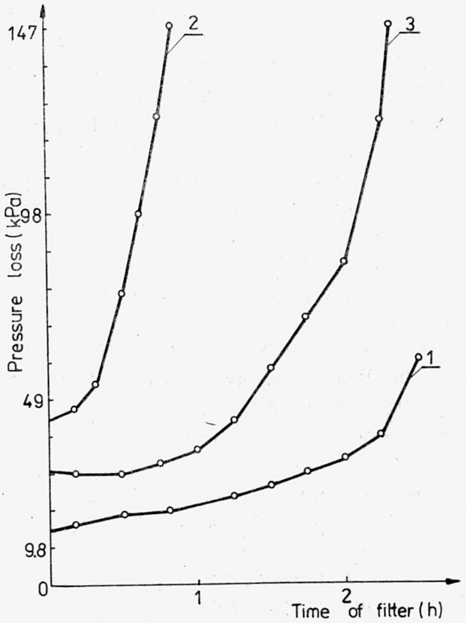

Fig. 10. Pressure loss in the course of the process

For explanations see fig. 9

Rys. 10. Spadek ciśnienia w trakcie procesu

Objaśnienia jak na rys. 9

3. To ensure a stable filter performance the polyurethane foams should be subject to precompression in the coalescer.

4. Polyurethane foam coalescers can be regenerated by mechanical compressing, which allows the reuse of the foams without deteriorating the efficiency of the treatment process.

REFERENCES

[1] Anufrieva N. M., Nesterova M. P., Vodnyje Resursy, No. 4 (1976), 149–153.

[2] Aurelle Y., Abadie A., Roques H., *Traitment par coalescence sur résines déophiles des eaux résiduaires contenant des hydrocarbures émulsionnés*, Centre Belge d'Etude et de Documentation des Eaux, mars 1973, No. 352, 108–122.

[3] Bhaudare M. V., Sen Gupta R., Mahasagar, Vol. 9, No. 1–2, 67–69, 1976.

[4] Canevari P., *Oil on the Sea*, New York 1969, p. 31.

[5] Chem. and Eng. News, Vol. 45 (1967), No. 41.

[6] Chieu I.N., Gloyna E.F., Schechter R.S., *Device for Evaluating Coalescence of Oil Emulsions*, Institute of the Environmental Engineering Division, 1977 April, 163–175.

[7] Gomółka E., Rybka J., *Foamed Polyurethane as Sorbent of Oil from Wastewater*, Second Inter. Conf., Lublin 1979, June 7–10, 40-1-41-10.

[8] Hupka I., Ph. D. thesis, Technical University of Gdańsk, 1978.

[9] Jarre W., Marx M., Wurmb R., *Polyurethanschäume mit hohen Ölab Sorptionsvermögen*, Die Angewandte Makromolekulare Chemie, 78 (1979), 67–74, No. 1258.

[10] Lozovskii D.S., Kailovič A., Kikteva V.I., Sevrjukov S.K., Chimija Technol. Topl. Masel, 1976 (11), 28–30.

[11] Olczyk W., *Poliuretany*, WNT, Warszawa 1973.

[12] Patent, West Germany, 1634188, 1971.

[13] Patent, France, 1534735, 1968.

[14] Patent, 96079, 1979.

[15] Patent, West Germany, 23036633, 1973.

[16] Polimery, 1973, 18 (6), 227–228.

[17] Romagnoli R.I., Berqlund R.L., *Polyurethane Foam Filtration*, Proc. Ind. Waste Conf., 1978 (publ. 1979), 33, 343–356.

[18] Tanker and Bulk Carriers, 1967, No. 5, p. 14.

[19] Turbeville I.E., *A Ferromagnetic Sorbent System for Oil Spill Recovery*, Proc. Ann Offshore Technol. Conf., 1976, 8, 3, 883–8.

[20] UK Patent, 1209607, 1970.

[21] US Patent, 3650406, 1972.

[22] US Patent, 3702657, 1972.

[23] US Patent, 3617552, 1971.

[24] UK Patent, 1210967, 1970.

[25] US Patent, 3608727, 1971.

[26] US Patent, 3539508, 1970.

[27] US Patent, 3617551, 1971.

[28] US Patent, 4111801, 1978.

KOALESCENCJA ZEMULGOWANYCH ŚCIEKÓW OLEJOWYCH PRZEZ ZŁOŻA PIANKOWEGO POLIURETANU

Przedstawiono zagadnienie rozbijania emulsji olej–woda. Olej zawarty w ściekach przemysłowych jest usuwany przez koalescencję na złożach poliuretanowych. Niektóre parametry koalescencji, właściwości koalescera i efektywność usuwania oleju ze ścieków przemysłowych zostały szczegółowo omówione. Dla ustabilizowanych mechanicznie emulsji olej–woda uzyskano 98%–99,5% oczyszczania. Stężenie oleju w odpływie ze złoża koalescyjnego wynosi zaledwie 5–10 ppm.

Wyniki doświadczeń, jak również fizykochemiczne właściwości poliuretanu, a zwłaszcza jego pojemność absorpcyjna w stosunku do oleju, przemawiają za zastosowaniem złoża z pianki poliuretanowej do oczyszczania zemulgowanych ścieków olejowych. Użycie złóż poliuretanowych daje obecnie bardzo dobre wyniki, a w przyszłości zakres ich zastosowań może jeszcze wzrosnąć.

KOALESZENZ VON EMULGIERTEN, ÖLHALTIGEN ABWÄSSERN DURCH EIN POLYURETHAN-SCHAUMBETT

Dargestellt wird das Problem des Aufschlusses der Emulsion Öl–Wasser. Öle, die in industriellen Abwässern enthalten sind, werden durch Koaleszenz auf Polyurethanbettfiltern zurückgehalten. Einige Faktoren der Koaleszenz, die Eigenschaften des Schaumbetts und die Beseitigungsrate werden eingehend

besprochen. Für mechanisch stabilisierte Öl–Wasser–Emulsionen erhielt der Verfasser eine 98–99,5% Abnahme. Die Ölkonzentration im Filterbettabfluß betrug nur 5–10 ppm.

Diese Ergebnisse, die physikalisch-chemische Eigenschaften des Polyurethans und besonders das absorptive Volumen Öl gegenüber, sprechen für die Anwendung eines Filterbetts aus Polyurethanschaum zur Reinigung von emulgierten, ölhaltigen Abwässern. Die Anwendungspalette wird in der Zukunft mutmaßlich noch reicher.

КОАЛЕСЦЕНЦИЯ ЭМУЛЬГИРОВАННЫХ МАСЛЯНЫХ СТОЧНЫХ ВОД ЧЕРЕЗ СЛОИ ПЕНОПОЛИУРЕТАНА

Представлен вопрос разбивания эмульсии масло–вода. Масло, содержащееся в промышленных сточных водах, удаляется посредством коалесценции на полиуретановых слоях. Подробно обсуждены некоторые параметры коалесценции, свойства коагулятора и эффективность удаления масла из промышленных сточных вод. Для механически стабилизированных эмульсий масло–вода было получено 98–99,5% очистки. Концентрация масла в стоке с коалесценционного слоя составляет лишь 5–10 млн$^{-1}$.

Результаты опытов, а также физикохимические свойства полиуретана, а в частности, его ёмкость поглощения по отношению к маслу убеждают о применении слоёв из пенополиуретана для очистки эмульгированных масляных сточных вод. Использование полиуретановых слоёв в настоящее время даёт очень хорошие результаты, а в будущем область их применения может ещё расшириться.