CHEMISTRY FOR PROTECTION
OF THE ENVIRONMENT 1987

Proceedings of the Sixth International Conference, Torino, Italy,
15–18 September 1987

Edited by

L. Pawlowski
Department of Water and Wastewater Technology, Technical University of Lublin,
20-618 Lublin, Poland

E. Mentasti
Department of Analytical Chemistry of the University of Torino, Italy

W.J. Lacy
9114 Cherrytree Drive, Alexandria, VA 22309, U.S.A.

C. Sarzanini
Department of Analytical Chemistry of the University of Torino, Italy

ABSORPTIVITY OF FIBROUS MATS
APPLIED FOR REMOVING SPILT OIL

J. DRELICH
J. HUPKA
B. GUTKOWSKI
Institute of Inorganic Chemistry and Technology, Technical University of Gdańsk, Poland

ABSTRACT

Capillary containment model has been proposed for theoretical assessment of sorbing capacity of fibrous mats in the sorbent-oil-air system. The influence of essential system properties like sorbent oleophilicity, apparent density and mat thickness is included.

Experimental data on sorbing capacity of randomly packed fibres remain in good agreement with the theoretical curve above certain packing density characteristic for sorbing material employed. With decreasing packing density growing discrepancies occur due to limited ability of oil to penetrate the entire volume of mat.

1. INTRODUCTION

Absorption by means of materials having an extended surface is a frequently used method for removing spilt oil from the surface of water or from ground. Sorbing materials find application in the shape of tampons, mats, cushions, endless bands and barriers [1, 2]. Beside tampons, mats are the predominantly encountered form of sorbents offered by specialised companies. They are made of synthetic fibres (polypropylene, polyethylene and polyester) [3–6], foamed polyurethanes and natural products like peat, cotton fibres, cellulose and kapok [4–8].

Most often the suitability of materials for removing spilt oil is characterised by the sorbing capacity. The sorbing capacity is defined as the ratio of mass of the gathered oil to the mass of sorbent. References quote many experimental data pertaining to the sorption capacity value for a variety of materials [4, 6, 8–11], but hardly any attempts can be found for its determination on a theoretical way. In the present study a dependence has been derived for the absorptivity of mats
2. THEORETICAL ABSORPTIVITY OF MATS

In order to determine absorptivity of mats the following assumptions have been made:

- the mat comes in contact with one liquid phase only and it does not sink,
- the oil remains in contact with the sorbent until a state of equilibrium is attained,
- a thin film of oil adheres to the external fragments of the mat and that is why the resulting increase in the mat dimensions can be neglected,
- the menisci formed in the capillary tubes are all of identical shape and have one radius of curvature only (Fig. 1A),
- the oil which is released at taking the mat out of the liquid is not to be considered as absorbed oil.

The quantity of liquid gathered in the free spaces in the mat amounts to:

\[ m = \frac{\pi d^2}{4} \rho_0 n \]  
\[ (1) \]

The capillaries are filled with oil from their base up to the level \( h \) (Fig. 1A).

The volume of oil contained above the level \( h \) is not given consideration in the dependence (1). When the mat gets lifted, losing its contact with the layer of oil, a lower meniscus is formed. Thus, the final quantity of collected liquid amounts to:

\[ m = \left( \frac{\pi d^2}{4} h - A_0 \right) \rho_0 n \]  
\[ (2) \]

where: \( A_0 \) is a correction factor (see Appendix).

The number capillaries in the mat can be determined on the basis of the empty space between the fibres (porosity of the mat):

\[ n = \frac{4V_0}{\pi d^2 H} = \frac{4\rho_0 (\rho_s - 1)}{\pi d^2 \rho_s H} \]  
\[ (3) \]

where: \( \rho_s \) is the packing density defined as

\[ \rho_s = \frac{m}{V_o} \]  
\[ (4) \]

From the definition of absorptivity:

\[ C = \frac{m}{\rho_s} \]  
\[ (5) \]

Substitution (2) and (3) into (5) results in:

\[ C = \frac{(\rho_s - \rho_0)(H - A)\rho_0}{\rho_s \rho_0 H} \]  
\[ (6) \]

where: \( A = \frac{4A_0}{\pi d^2} = \left( \frac{\rho_s - \rho_0}{\rho_s \cos^2 \theta} \right) \left( \frac{2(1 - \sin \theta)(1 - \sin \theta)}{3 \cos^2 \theta} - 1 \right) \)

In the case when the mat is filled with oil up to its total height then:

\[ C = \frac{(\rho_s - \rho_0)(H - x - A)}{\rho_s \rho_0 H} \]  
\[ (7) \]

where: \( x = \frac{2(\rho_s - \rho_0)(1 - \sin \theta)}{\rho_s \cos^2 \theta} \)

Whenever \( h \gg A \) and \( h \gg x \) the equation (6) is reduced to a simple dependence as derived earlier [2]:

\[ C = \frac{(\rho_s - \rho_0)\rho_0}{\rho_s \rho_0} \]  
\[ (8) \]
The driving force $\Delta P$ under the influence of which the oil penetrates the mat, is the result of capillary pressure stimulating the movement of the liquid in the capillary and hydrostatic pressure which inhibits this movement (Fig. 1A):

$$\Delta P = P_h - P_a$$  \hspace{1cm} (9)

After introducing $P_h$ from the Laplace equation for a circular capillary with a spherical meniscus and $P_a$ from the hydrostatic pressure equation a dependence for the capillary rise is obtained:

$$h = \frac{4\sigma_0 \cos \Theta - \rho g}{d \rho_0 g}$$  \hspace{1cm} (10)

Thus, the absorptivity of the mat amounts to:

$$C = \frac{(\rho_s - \rho_a)\rho_0}{\rho_s \rho_0 H} \left[ \frac{4\sigma_0 \cos \Theta - (\rho_s - \rho_a)\rho g}{(\rho_s - \rho_a)\rho g} - A \right]$$  \hspace{1cm} (11)

In such case it is more advantageous to apply equation (7). In the case when $\Delta P = 0$:

$$C = \frac{(\rho_s - \rho_a)\rho_0}{\rho_s \rho_0 H} \left[ \frac{4\sigma_0 \cos \Theta}{\rho_s - \rho_a} - A \right]$$  \hspace{1cm} (12)

Further herein discussed is the effect of the principal factors on the absorptivity value of mats on the basis of the equations (7) and (12).

3. EXPERIMENTAL

3.1. Experimental System

In order to correlate the theoretical and experimental absorptivity laboratory measurements were carried out. The tests employed the KS–1 sorbent, one of the three products (having the lowest absorbing capacity) coming from recovered cord from worn automobile tyres [12], and commercial polypropylene-polyester fibres. The basic data pertaining to these materials are given in Tab. 1. The oils subjected to absorption are characterized in Tab. 2.

The mat was substituted by a box made of perforated sheet metal being a cuboid with a rectangular base of 0.15 x 0.10 m, ensuring dimensional stability, and filled with the material under test. A weighed sample of the material was placed in the box and pressed by means of a perforated cover to secure desired packing density ($\rho_s$) at height (H).

The box substituting mat was contacted with the oil layer for a period of time ensuring equilibrium saturation. Light oil required several minutes to saturate the sorbent while for the heavy oil of viscosity 0.3 Pas the penetration time was extended to a few hours in densely packed sorbent. Then, the box was lifted and left for possible dripping for 2 minutes (30 seconds in the case of hexane), cleaned to remove oil from the bottom surface and weighed. The sorbent was removed and the box weighed again. The absorptivity was calculated on the basis of mass difference.

**Tab. 1. Summary of sorbents characteristics**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fraction (weight)</th>
<th>Diameter $10^{-6}$ m</th>
<th>Mean diameter $10^{-6}$ m</th>
<th>Lenght $10^{-3}$ m</th>
<th>Mean density of sorbent $kg m^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamide fibres</td>
<td>50</td>
<td>28–32</td>
<td>21</td>
<td>5–25</td>
<td>1500</td>
</tr>
<tr>
<td>Viscose fibres</td>
<td>45</td>
<td>12–16</td>
<td>25</td>
<td>5–25</td>
<td>1035</td>
</tr>
<tr>
<td>Rubber particles</td>
<td>5</td>
<td>10–1000</td>
<td>200</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Polypropylene fibres</td>
<td>75</td>
<td>24–36</td>
<td>31</td>
<td>50–60</td>
<td>1035</td>
</tr>
<tr>
<td>Polyester fibres</td>
<td>25</td>
<td>50–60</td>
<td>31</td>
<td>50–60</td>
<td>1035</td>
</tr>
</tbody>
</table>

**Tab. 2. Summary of oil properties at temperature 293 K**

<table>
<thead>
<tr>
<th>Oil</th>
<th>Density $kg m^{-3}$</th>
<th>Viscosity $mPa.s$</th>
<th>Surface tension $Nm^{-1}$</th>
<th>Polyamide fibre</th>
<th>Viscose fibre</th>
<th>Polypropylene fibre</th>
<th>Polyester fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>660</td>
<td>0.40</td>
<td>18.4</td>
<td>5–10</td>
<td>5</td>
<td>10–15</td>
<td>5</td>
</tr>
<tr>
<td>Diesel oil</td>
<td>832</td>
<td>4.23</td>
<td>34.5</td>
<td>9–12</td>
<td>5</td>
<td>6–12</td>
<td>5</td>
</tr>
<tr>
<td>Lux 10 engine oil</td>
<td>880</td>
<td>344.00</td>
<td>32.5</td>
<td>5</td>
<td>5</td>
<td>10–15</td>
<td>5</td>
</tr>
</tbody>
</table>

4. RESULTS AND DISCUSSION

4.1. Packing Density

Theoretical curves and experimental points have been traced in Fig. 2 and Fig. 3 on the basis of the equation (12) and at a packing density guarantying $h < H + x$ or equation (7) for $h < H + x$.

The method of determining the equivalent diameters of substitute model capillaries is given in the Appendix. The proposed model remains in good conformity with the experimental data. A change in the packing density influences the distance between the fibres. The maximum absorptivity is attained at a sufficiently low
\( \rho_u \), after which it decreases. A capillary gets filled only when a sufficiently high packing density is ensured. Otherwise only bridges appear between the fibres, and the remaining part of the material is left unsaturated.

The mat packing density should not be lower than the critical value \( (\rho_{u,cr}) \), under which the mat will not be filled at its total height (i.e. for \( h < H + x \)). An increase in the packing density above \( \rho_{u,cr} \) does not result in any better use of the empty spaces in the mat, rather the potential absorptivity drops. The critical values of the pp. fibres packing density are contained in the range of 20–30 kg/m\(^3\), and for KS–1 between 130–190 kg/m\(^3\). The possibility of attaining higher absorptivity by pp sorbent follows from the fact that KS–1 has much wider distribution of interfilament spacings. Thus, it is advantageous to use sorbents with a highly extended surface and composed if elements of uniform size. It may be concluded from the wetting angle values given in Tab. 2 that the oils used in the tests showed a similar affinity to the same kind of fibres. The differences in the absorptivity for the particular oils follow rather from the differences in their density and surface tensions. In compliance with the dependence (7) an increase in the oil density has a favourable effect on the absorptivity value, but the surface tension effects the height of the capillary rise (dependence 10) appearing, above all, in the range of low packing densities (of less than \( \rho_{u,cr} \)).

### 4.2. Thickness of the Mat

The diagram in Fig. 4 which represents the sorbent absorptivity versus the mat thickness shows that a maximum is attained and that the absorptivity quickly decreases with the diminishing thickness of the mat.

In the case of a small mat thickness the meniscus curvature has a predominant effect on the volume of the oil absorbed, and the absorptivity, calculated from dependence (7) may even approach 0. In practice thin mats are effective in gathering highly viscous oils, but the sorbing mechanism is different from the capillary containment discussed here. The critical thickness of the mat below which a rapid fall in the absorptivity takes place, corresponds to such a capillary rise (\( H \approx h \)) which can be attained at the existing empty space cross-sections between the fibres in the mat.

The quantity of oil absorbed by the mat and then released by dripping is a function of mat orientation in space as shown in Fig. 5. Low viscous oil (i.e.
Fig. 4. Influence of mat thickness on absorbing capacity. Experimental values constitute mean from two or three runs under similar conditions.

quickly migrating in the mat) is released easily when the mat changes its position from horizontal to vertical. In such case the content of oil above the capillary rise (residual saturation) amounts from 6 to 10 per cent in the state of equilibrium. The more heterogeneous is the structure of the mat the higher is the residual saturation [13].

4.3. Properties of Contacting Phases

Fig. 6 shows the dependence of the KS-1 sorbent absorptivity on the density of oil for changing packing densities.

The theoretical course was determined on the basis of the dependence (7). Changes in the density of oil were obtained by preparing mixtures of hexane with engine oil Lux 10 in various proportions. According to the results the effect of oil density is negligible.

The theoretical course of the \( C = f(\rho_s) \) is shown in Fig. 7.

The effect of the sorbent density is insignificant and it may be neglected. However, there is a great effect of the sorbent density on the packing density. Thus, it is convenient to apply materials with the lowest possible density. The connected effect of the surface properties of oil and the sorbent may be expressed by the Young-Dupre equation:

\[
\sigma_s - \sigma_{so} = \sigma_0 \cos \Theta
\]  

(13)

where the product of \( \sigma_0 \cos \Theta \) is an index for the wettability in the system involved. The effect of \( \sigma_0 \cos \Theta \) on the absorptivity value is shown by the dependences derived. It is only in the case of favourable wettability of the material with oil (also in the presence of an aqueous phase) that a capillary rise guarantying the maximum capacity of the mat is attained. Commercial sorbents possess high oil affinity which in most cases ensure complete mat saturation with oil.

5. CONCLUSION

The capillary filling model proposed for determination of the absorptivity of mats applied for removing spilt oils is in good conformity with laboratory data for the KS-1 sorbent and polypropylene-polyester fibrous material. Availability of characteristics of the sorbing material as well as of the oil to be removed is sufficient for calculating the absorptivity of the mat by the following formula:

\[
C = \frac{(\rho_s - \rho_o)(h - A)\rho_o}{\rho_s \rho_o H}
\]

The derived dependence makes it possible to determine the optimum packing density for the material involved and the oil in relation to the absorptivity value.
Fig. 6. Influence of oil density on absorbing capacity

In the case of polypropylene-polyester fibrous material the highest values of absorptivity (15 to 28 kg kg⁻¹) were attained at the packing density range of 20 to 30 kg m⁻³, and in the case of the KS-1 sorbent absorptivity ranged between 130 and 190 kg m⁻³ (C = 2.6 – 4.6 kg kg⁻¹) for the oils under investigation.

6. APPENDIX

6.1. Volume of Liquid Collected in Capillaries

The volume of liquid entrapped by the capillary forces and expressed by means of the equation (1) must be corrected because of the presence of two menisci Fig. 1A. The correction factor amounts to: (Fig. 8)

\[ A_0 = \left( \frac{\pi R_x^2 - \frac{1}{2} \pi x^3}{\cos \Theta} \right) - (\pi R_x^2 - \pi R_x^2 + \frac{1}{2} \pi x^3) = 2\pi R_x^2 + \frac{1}{2} \pi x^3 - \pi R_x^2 \]  

(1A)

In addition:

\[ R = \frac{r}{\cos \Theta} \]  

(2A)

Fig. 7. Absorbing capacity as a function of sorbing material density

\[ \pi = \frac{r (1 - \sin \Theta)}{\cos \Theta} \]  

(3A)

After substituting (2A) and (3A) into (1A) we have:

\[ A_0 = \frac{\pi r^3 (1 - \sin \Theta)}{\cos \Theta} \left( \frac{2(1 - \sin \Theta)(4 - \sin \Theta)}{3 \cos^2 \Theta} - 1 \right) \]  

(4A)

6.2. Capillary Substitute Diameter

Theoretical Diameter

The substitute diameter of the space between the fibres in the mat have been assumed to be equal to four times the value of the hydraulic radius:

\[ d_x = 4 r_n = \frac{4 S}{B} \]  

(5A)

where:

\[ S = S_M - \frac{\pi d^2_n}{4} n_w \]  

(6A)

- capillary cross-section area

\[ B = \pi d_w n_w \]  

(7A)
Fig. 8. Geometrical relations in spherical meniscus

- perimeter of the elements of packing forming the capillary in cross-section $S$

The number of fibres $n_w$ was calculated from the dependence (4) by substituting the following dependences for $m_s$ and $V_s$:

$$m_s = \frac{\pi d_w^2}{4} H n_w \rho_s$$  \hspace{1cm} (8A)

$$V_s = S_M H$$  \hspace{1cm} (9A)

The result being:

$$n_w = \frac{4 \rho_s S_M}{\pi d_w^2 \rho_s}$$  \hspace{1cm} (10A)

By introducing (10A), (6A) and (7A) into (5A) we have:

$$d_s = \frac{(\rho_s - \rho_u) d_w}{\rho_u}$$  \hspace{1cm} (11A)

Experimental Diameter

The distribution of interfilament distances was determined experimentally. A perforated cardboard box packed with fibres was submersed in a polymethylacrylate resin and then dried at 150°C.

Fig. 9. Equivalent diameter of interfilament spacings as a function of packing density. Due to presence of rubber particles it is reasonable not to draw the theoretical curve for sorbent KS-1

Fragments were cut off from the solidified sorbent-resin block for taking microscopic photographs. The surface under investigation was measured on the pictures obtained and the number of fibres counted. The experimental mean substitute diameters in the mat (Fig. 9) were determined from the dependence (5A) by introducing (6A) and (7A).

**SYMBOLS**

$A_0$ - correcting factor [m$^2$]
A - correcting factor, $A = \frac{A_0}{\pi R}$ [m]
B - capillary perimeter [m]
C - absorbing capacity [kg kg$^{-1}$]
d$_s$ - fibre diameter [m]
d$_w$ - equivalent diameter of a capillary [m]
g - acceleration of gravity $g = 9.81$ [ms$^{-2}$]
h - capillary rise height [m]
H – thickness of mat [m]

m – mass of mat [kg]

m – mass of oil [kg]

n – number of capillaries

n – number of fibres

P – capillary pressure [Pa]

P – hydrostatic pressure [Pa]

ΔP – pressure difference at oil-interface [Pa]

r – capillary radius [m]

R – meniscus radius [m]

S – capillary cross-sectional area [m^2]

S – surface areas of a mat [m^2]

V – mat volume [m^3]

z – height of meniscus [m]

θ – equilibrium contact angle [deg]

θ – dynamic contact angle [deg]

ρ – oil density [kg m^-3]

ρ – density of sorbing material [kg m^-3]

ρ – packing density of a mat [kg m^-3]

σ – surface tension of oil [Nm^-1]

σ – surface tension of sorbing material [Nm^-1]

σ – sorbent-oil interface tension [Nm^-1]

REFERENCES


2. Hupka J., The determination of the sorbing capacity of sorbents used to clean-up oil spills, ibid., 261, 35, 1981.


