Adsorption Method of Emulsion Coolants Separation

Part I. Study on Sewage Treatment on Carbon-Lime Bed

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Abstract: The effectiveness of oil sewage purification by filtration on carbon-lime bed; the voluminal ratio of carbon ash to waste lime was equal to Vc/Vca = 0.375; 0.5; 0.625. The ether extract, COD, absorbance and inorganic contaminations with components of bed such as Ca\textsuperscript{2+}, Cl\textsuperscript{-} were determined. The effectiveness of sewage purification increased as the quantity of sewage treated was increased. Absorbance of the purified sewage was similar to that of distilled water filtered on the bed.

Key Words: Sewage Purification, Oil Sewages, Adsorbent, Carbon-lime Bed, Emulsion, Permeability of Bed

Introduction
According to worldwide trend concerning the environment protection, more and more attention is paid to the problem of purity of waters almost in all countries in the world.

Emulsions containing often excessive amounts of oil non-eliminated in municipal sewage treatment plants penetrate to the surface waters, rivers and lakes causing huge losses.

Therefore, disposal of contamination is required in order to reduce ecological hazard. A portion of emulsion is poured out in raw state what causes clogging of sewage system, installations in municipal sewage treatment plant and degradation of surface and deep waters.

Oily impurities in industrial wastes can occur in the following forms (Dakovic, 1985):
- non-emulsified (free oil in the form of large separate drops ascending towards the liquid surface),
- oil emulsion where oil occurs in the form of drops smaller than 50μm,
- dissolved.

Many chemical, physical, physicochemical and biological methods (US, 1989; Aurelle et al., 1973; Aurelle et al., 1978; Bartkiewicz, 1974; Bartkiewicz, 1976; Chojnacki and Bartkiewicz, 1972; Chojnacki, 1965; Humenick and Bavis, 1978; Lendzion, 1990; Lindh, and Dahlén, 1989; Małaczyński, 1979; Mańczak, 1972; Mayo, 1960; Meibaum and Stasch, 1978; Meink et al., 1975; Strzelczyk, 1974; Urbański, 1981) such as coagulation, filtration, ultra-filtration, adsorption, coalescence or inverted osmosis (Bal, 1988; Bodzek et al., 1981; Bukowski and Grudzińska, 1975; Koziorowski, 1980; Meink et al., 1975; Pysiak et al., 1992) are applied for destabilization of emulsion.

Application of a single method e.g. flotation, flocculation or coalescence do not lead to the satisfactory decrease in oil content in waste i.e. to the required statutory level. Only appropriately selected system of operations can ensure an effective and concurrent, with respect to economy, sewage treatment (SU, 1985; HU, 1987 and 10, 1988).

Separation of the components is particularly difficult in the case of oil emulsions obtained by mixing the mineral oils with water and applied mainly in engineering, metallurgical and automotive industries as coolants during machining and plastic forming.

They contain oil as a phase well dispersed in dispersive medium i.e. in water and they are classified to emulsions of "oil in water" type. Concentration of emulsion oil in water can be various within the range from 3 to 20% depending on its application. Modern emulsions contain additionally many toxic components such as: surface-active agents, inhibitors, anti-foaming agents, bactericides an other. After period of use in technological process lasting from several days to several weeks, emulsions are "ageing" and they must be removed from the systems. The reason of emulsion ageing is the most often biological decay under the anaerobic conditions resulting in unpleasant odour. The used emulsion coolants are especially burdensome wastes. High content of oil cause high COD and BOD values and increased amount of ether extract.

In the light of facts presented above, the studies on inquiring into effective method of management of the used emulsion coolants seems to be well-grounded.

Materials and Methods
The emulsifying oil – VECO EMULEX ES-12 was used for studies on sewage treatment capacity on carbon – waste lime bed. It is a conventional coolant being the mixture of paraffin and mineral oils, emulsifiers, antitrust agents and bactericides. After mixing with water, it forms milky-white emulsion, odourless, characterized by high stability, good antitrust properties and it is safe from dermatological point of view. The oil – water voluminal ratio applied in our studies was 1:30 and emulsion was used for 2 months.

Adsorption was conducted on granulated fertilizing chalk in composition with carbon ash at the following ash – chalk ratios:
- Vc/Vca = 0.375
- Vc/Vca = 0.5
- Vc/Vca = 0.625

The experiments were carried out in the column (ID = 100 mm, height L = 700 mm) equipped with porous bottom.

The bed height in column was l0 = 400 mm, however, the waste dosage was kept on a constant level above the bed h0 = 50 mm.

\[ u = \frac{V}{\pi D^2 \tau} = k \cdot \frac{h_0 + l_0}{l_0} \]

Filtration rate \( u \) was determined by measuring the filtrate stream (purified waste) i.e. filtrate volume \( V \) in cylinder, collected in time \( \tau \) measured by stop-watch.
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Studies were carried out in a column (internal diameter \( D = 50 \) mm and height \( L = 700 \) mm) with porous bottom; height of bed was \( L = 640 \) mm. The constant emulsion level equal to the bed height was kept \((H = H_0 + L = L)\); for \( H_0 = 0 \) and thus, the stream of emulsion flowing in was equal to the stream of the filtrate flowing out.

Permeability of bed \( k \) is equal to linear velocity \( u \) for \( H = L \):

\[
\Delta P = \frac{200 \mu L}{d^2} \frac{\varphi (1-e)}{e^3}
\]

Hence

\[
u = \frac{H}{L} \frac{\rho g d^2 e^3}{200 \eta \varphi (1-e)^2} = \frac{H}{L} \cdot k = k
\]

Linear velocity \( u \) of filtration

\[
\frac{V}{D^2 r}
\]

was determined by measurement of the filtrate voluminal stream (purified sewage)

\[
\frac{V}{r}
\]

The effectiveness of sewage purification was determined by measurements of:

- content of substances extracted by petroleum ether, \([\text{mg/dm}^3]\)
- acidity of coolant and alkalinity of purified sewage, \([\text{mmole/dm}^3]\)
- chemical Oxygen Demand (COD), \([\text{mg O}_2/\text{dm}^3]\)
- absorbance of purified sewage and for comparison raw sewage (emulsion) and distilled water filtered by carbon-lime bed,
- content of calcium and chloride ions in purified sewage filtered by bed being the composition of carbon ash and lime from soda processing \([\text{mmol/dm}^3]\).

The composition of the waste lime from soda industry was as follows:

- \( \text{CaCO}_3 \) - 20,5 \%
- \( \text{Ca(OH)}_2 \) - 43,6 \%
- \( \text{CaCl}_2 \) - 6,0 \%
- \( \text{H}_2\text{O} \) - 29,9 \%

Results and Discussion

Examples of results are presented in Tables 1 and 2 and Figures 1 – 5.

Table 1: Results of the Studies on Effectiveness of Emulsion Purification on Carbon-lime Bed (voluminal ratio of carbon ash to lime \( V_c/V_c = 0,375 \))

<table>
<thead>
<tr>
<th>No.</th>
<th>Type of sample</th>
<th>Filtration rate ( U ) [m(^3)/m(^3)]</th>
<th>Permeability ( k ) [m(^3)/m(^3)]</th>
<th>Alkalinity of sample ( C_{OH}^- ) [mmole/( r\text{dm}^3)]</th>
<th>Content of ( \text{Ca}^{2+} ) ( C_{Ca^{2+}} ) [mmole/( r\text{dm}^3)]</th>
<th>Content of ( \text{Cl}^- ) ( C_\alpha^- ) [mmole/( r\text{dm}^3)]</th>
<th>Ether extract [mg/dm(^3)]</th>
<th>COD [mg/dm(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>emulsion</td>
<td>-</td>
<td>-</td>
<td>3,9</td>
<td>( [H^+] = 3,9 )</td>
<td>-</td>
<td>-</td>
<td>8196,4</td>
</tr>
<tr>
<td>1</td>
<td>purified sewage</td>
<td>1084</td>
<td>4,2 \cdot 10^{-4}</td>
<td>4,2 \cdot 10^{-4}</td>
<td>9,4</td>
<td>37,6</td>
<td>64,2</td>
<td>160,8</td>
</tr>
<tr>
<td>2</td>
<td>purified sewage</td>
<td>1068</td>
<td>4,04 \cdot 10^{-4}</td>
<td>4,04 \cdot 10^{-4}</td>
<td>9,6</td>
<td>38,4</td>
<td>38,6</td>
<td>96,7</td>
</tr>
<tr>
<td>3</td>
<td>purified sewage</td>
<td>1082</td>
<td>3,92 \cdot 10^{-4}</td>
<td>3,92 \cdot 10^{-4}</td>
<td>9,8</td>
<td>39,2</td>
<td>24,5</td>
<td>61,4</td>
</tr>
<tr>
<td>4</td>
<td>purified sewage</td>
<td>1285</td>
<td>2,8 \cdot 10^{-4}</td>
<td>2,8 \cdot 10^{-4}</td>
<td>10,0</td>
<td>40,0</td>
<td>18,0</td>
<td>45,7</td>
</tr>
<tr>
<td>5</td>
<td>purified sewage</td>
<td>1445</td>
<td>2,19 \cdot 10^{-4}</td>
<td>2,19 \cdot 10^{-4}</td>
<td>10,7</td>
<td>42,8</td>
<td>13,7</td>
<td>34,3</td>
</tr>
<tr>
<td>6</td>
<td>purified sewage</td>
<td>1665</td>
<td>1,68 \cdot 10^{-4}</td>
<td>1,68 \cdot 10^{-4}</td>
<td>11,1</td>
<td>44,4</td>
<td>10,8</td>
<td>27,1</td>
</tr>
<tr>
<td>7</td>
<td>purified sewage</td>
<td>1932</td>
<td>1,23 \cdot 10^{-4}</td>
<td>1,23 \cdot 10^{-4}</td>
<td>12,2</td>
<td>48,8</td>
<td>10,6</td>
<td>26,6</td>
</tr>
</tbody>
</table>

Table 2: Dependence Between Effectiveness of Sewage Purification and Permeability of Bed with Respect to Its Composition

<table>
<thead>
<tr>
<th>Bed (v/v) ( V_c/V_c )</th>
<th>Filtration rate ( U ) [m(^3)/m(^3)]</th>
<th>Alkalinity of sample ( C_{OH}^- ) [mmole/( \text{dm}^3)]</th>
<th>Content of ( \text{Ca}^{2+} ) ( C_{Ca^{2+}} ) [mmole/( \text{dm}^3)]</th>
<th>Content of ( \text{Cl}^- ) ( C_\alpha^- ) [mmole/( \text{dm}^3)]</th>
<th>Ether extract [mg/dm(^3)]</th>
<th>COD [mg/dm(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,375</td>
<td>1,23 \cdot 10^{-4}</td>
<td>37,6-50,8</td>
<td>26,6-160,8</td>
<td>18,0-489,4</td>
<td>23,2-53,6</td>
<td>78,9-203,7</td>
</tr>
<tr>
<td>0,500</td>
<td>1,15 \cdot 10^{-4}</td>
<td>26,4-40,8</td>
<td>32,1-169,8</td>
<td>46,0-556,3</td>
<td>29,6-108,8</td>
<td>112,4-380,8</td>
</tr>
<tr>
<td>0,625</td>
<td>3,47 \cdot 10^{-5}</td>
<td>26,4-44,0</td>
<td>28,6-207,9</td>
<td>29,5-762,0</td>
<td>30,1-91,2</td>
<td>114,4-328,3</td>
</tr>
</tbody>
</table>
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Fig. 1: Dependence between Organic Substance Content (ether extract) on Amount of Cold Purified Sewage in Carbon-lime Bed $V_c/V_{ca} = 0.375$

Fig. 2: Dependence between Filtration Rate and Amount of Cold Purified Sewage in Carbon-lime Bed $V_c/V_{ca} = 0.375$

Fig. 3: Absorbance of Purified Sewage in Carbon-lime Bed $V_c/V_{ca} = 0.375$ (7 litres)
Fig. 4: Absorbance of Emulsion

Fig. 5: Absorbance of Distilled Water Passed Through Carbon-lime Bed
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Absorbance of the individual filtrate samples was equal to (after 7 litres of filtrate have passed through the bed):

- \( V_c / V_{Ca} = 0.375 \) mean absorbance value was \( A = 0.03 \)
- \( V_c / V_{Ca} = 0.50 \) mean absorbance value was \( A = 0.035 \)
- \( V_c / V_{Ca} = 0.625 \) mean absorbance value was \( A = 0.04 \)

On the basis of results presented in Table 2 for the individual compositions of bed tested within the range \( V_c / V_{Ca} = 0.375 - 0.625 \), it results that:

- sewage purification during filtration through the bed occurs as a consequence of coagulation of emulsion, coalescence of oil drop in bed ducts and oil adhesion to carbon-lime bed
- carbon-waste lime bed at the ratio \( V_c / V_{Ca} = 0.375 \) is characterized by the highest effectiveness of sewage purification and simultaneously the highest permeability
- the degree of purification increase during filtration of sewage i.e. decrease in ether extract quantity and simultaneously decrease of bed permeability occur in a consequence of decomposition of adsorbent grains during filtration what results in increase of adsorption surface and flow through the bed, the more so that the intergrain ducts are clogged up with adsorbed oil
- purified sewage has alkaline reaction as a result of dissolution of Ca(OH)\(_2\) and CaCO\(_3\) contained in bed and it is contaminated with Cl\(^-\) ions originated from dissolution of CaCl\(_2\)
- absorbance of purified sewage samples shows the amount of impurities (after comparison between absorbance of the initial emulsion and distilled water filtered through the bed) and it proves about effectiveness of their purification; absorbance of purified samples is similar to that of distilled water filtered through carbon – waste lime bed
- an effect of the ratio \( V_c / V_{Ca} \) in bed on effectiveness of purification is illustrated by absorbance of purified sewage samples for: \( V_c / V_{Ca} = 0.375 \) \( A = 0.03 \); \( V_c / V_{Ca} = 0.50 \) \( A = 0.035 \); \( V_c / V_{Ca} = 0.625 \) \( A = 0.04 \).

The used bed requires regeneration in order to avoid formation of carbon-lime-oil heaps.

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