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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 $V_c/V_{Ca} = 0{,}375; 0{,}5; 0{,}625$. The ether extract, COD, absorbance and inorganic contaminations with components of bed such as Ca^{+2}, Cl^- 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 oil.

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 Dahlen, 1989; Małaczyński, 1979; Mańczak, 1972; Mayo, 1960; Meibaum and Stasch, 1978; Meinck *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; Meinck *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 IO, 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, antirust agents and bactericides. After mixing with water, it forms milky-white emulsion, odourless, characterized by high stability, good antirust 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:

- $V_c/V_{Ca} = 0{,}375$
- $V_c/V_{Ca} = 0{,}5$
- $V_c/V_{Ca} = 0{,}625$

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 l_o = 400 mm, however, the waste dosage was kept on a constant level above the bed h_o = 50 mm.

$$u = \frac{V}{\frac{\pi}{4} D^2 \tau} = k \cdot \frac{h_o + l_o}{l_o}$$

Filtration rate u was determined by measuring the filtrate stream (purified waste) i.e. filtrate volume V in cylinder, collected in time τ measured by stop-watch.

Studies were carried out in a column (internal diameter D = 50 mm and height L_0 = 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:

$$\Delta P = H\rho g = \frac{200\eta u L}{d_z^2} \cdot \frac{\varphi^2(1-\varepsilon)^2}{\varepsilon^3}$$

Hence

$$u = \frac{H}{L} \cdot \frac{\rho g d_z^2 \varepsilon^3}{200\eta\varphi^2(1-\varepsilon)^2} = \frac{H}{L} \cdot k = k$$

Linear velocity ***u*** of filtration

$$u = \frac{V}{\frac{\pi}{4} D^2 \tau}$$

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

$$\dot{V} = \frac{V}{\tau}$$

i.e. volume *V* of filtrate in cylinder obtained in time τ measured by stop-watch.
The effectiveness of sewage purification was determined by measurements of:

- content of substances extracted by petroleum ether, [mg/dm³]
- acidity of coolant and alkalinity of purified sewage,[mmole/dm³]
- chemical Oxygen Demand (COD), [mg O_2/dm³]
- 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 [mmol/dm³].

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

- $CaCO_3$ - 20,5 %
- $Ca(OH)_2$ - 43,6 %
- $CaCl_2$ - 6,0 %
- H_2O- 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 Vc/Vc_a = 0,375)

No.	Type of sample	Filtration rate U		Permeability k	Alkalinity of sample C_{OH^-}		Content of Ca^{+2} C_{Ca+2}		Content of Cl^- C_{Cl^-}		Ether extract	COD
		S [cm³]	[m³/m²h]	[m³/m²h]	[ml] HCl	[mmole/dm³]	[ml] EDTA	[mmole/dm³]	[ml] $AgNO_3$	[mmole/dm³]	[mg/dm³]	[mgO₂/dm³]
0	emulsion	-	-	-	3,9	$[H^+]$=3,9	-	-	-	-	8196,4	28687,4
1	purified sewage	1084	$4,2 \cdot 10^{-4}$	$4,2 \cdot 10^{-4}$	9,4	37,6	64,2	160,8	98,2	489,4	53,6	203,7
2	purified sewage	1068	$4,04 \cdot 10^{-4}$	$4,04 \cdot 10^{-4}$	9,6	38,4	38,6	96,7	50,8	252,7	46,4	176,3
3	purified sewage	1082	$3,92 \cdot 10^{-4}$	$3,92 \cdot 10^{-4}$	9,8	39,2	24,5	61,4	23,5	116,3	42,4	148,4
4	purified sewage	1285	$2,8 \cdot 10^{-4}$	$2,8 \cdot 10^{-4}$	10,0	40,0	18,0	45,7	13,4	65,9	41,6	166,4
5	purified sewage	1445	$2,19 \cdot 10^{-4}$	$2,19 \cdot 10^{-4}$	10,7	42,8	13,7	34,3	8,2	39,9	35,2	123,2
6	purified sewage	1665	$1,68 \cdot 10^{-4}$	$1,68 \cdot 10^{-4}$	11,1	44,4	10,8	27,1	5,4	26,0	32,8	120,5
7	purified sewage	1932	$1,23 \cdot 10^{-4}$	$1,23 \cdot 10^{-4}$	12,2	48,8	10,6	26,6	3,8	18,0	23,2	78,9

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

Bed (v/v) Vc/Vc_a	Filtration rate	C_{OH^-}	C_{Ca+2}	C_{Cl^-}	Ether extract	COD
	m³/m²h	mmole/dm³	mmole/dm³	mmole/dm³	mg/dm³	mg/dm³
0,375	$1,23*10^{-4}$-$4,2*10^{-4}$	37,6-50,8	26,6-160,8	18,0-489,4	23,2-53,6	78,9-203,7
0,500	$1,15*10^{-6}$-$2,39*10^{-4}$	26,4-40,8	32,1-169,8	46,0-556,3	29,6-108,8	112,48-380,8
0,625	$3,47*10^{-6}$-$1,17*10^{-4}$	26,4-44,0	28,6-207,9	29,5-762,0	30,1-91,2	114,4-328,3

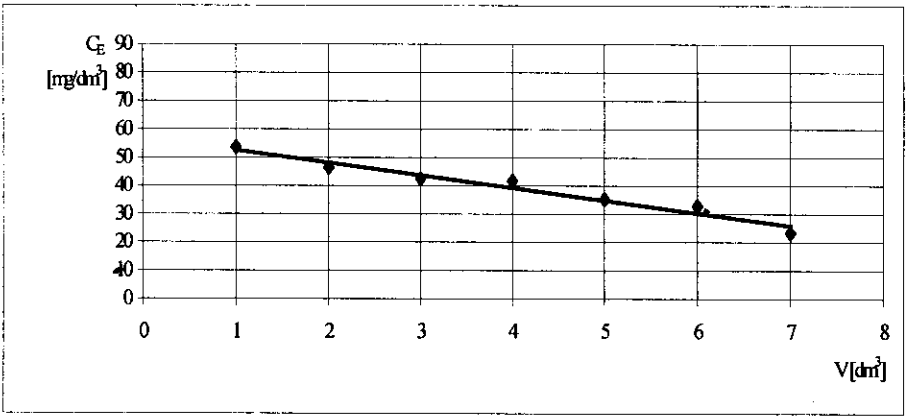

Fig. 1: Dependence Between Organic Substance Content (ether extract) on Amount of Cold Purified Sewage in Carbon-lime Bed Vc/Vca = 0,375

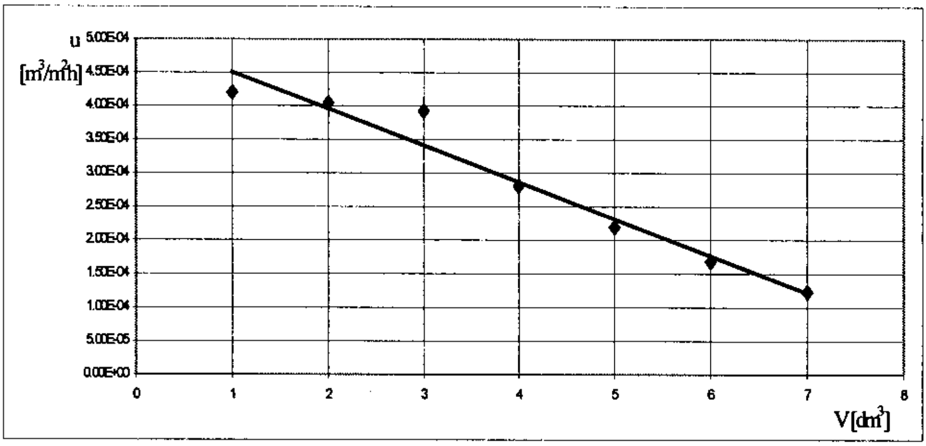

Fig. 2: Dependence Between Filtration Rate and Amount of Cold Purified Sewage in Carbon-lime Bed Vc/Vca = 0,375

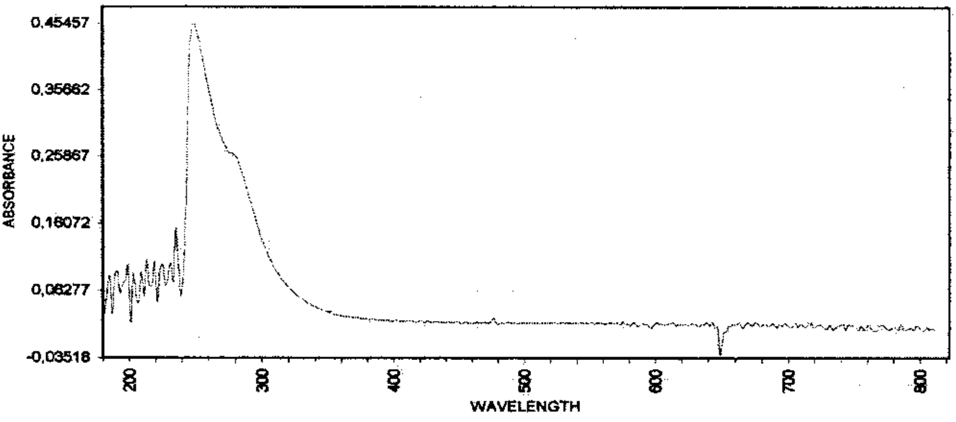

Fig.3: Absorbance of Purified Sewage in Carbon-lime Bed Vc/Vca = 0,375 (7 litres)

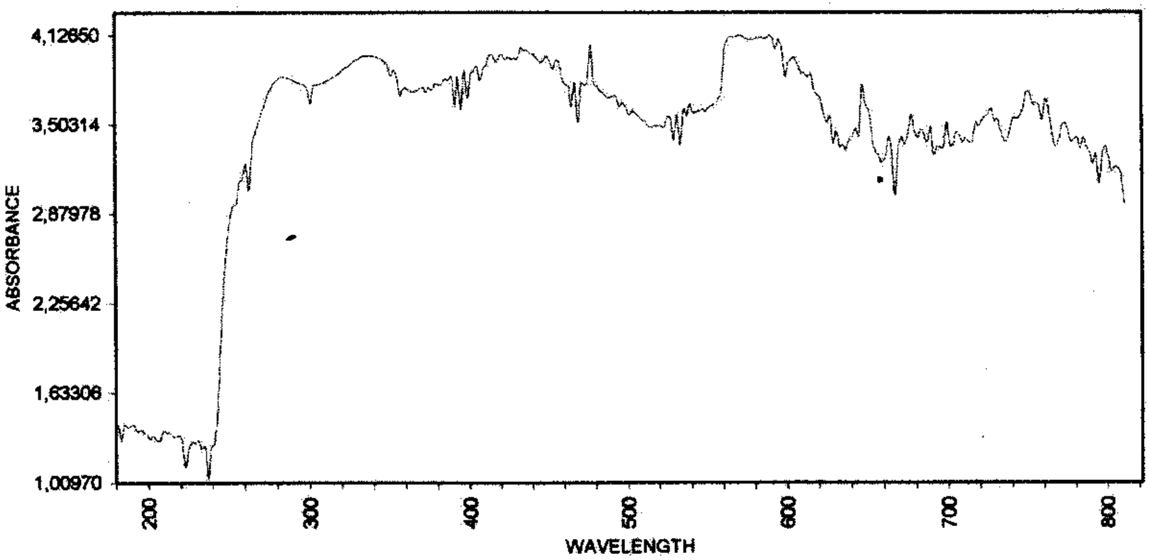

Fig. 4: Absorbance of Emulsion

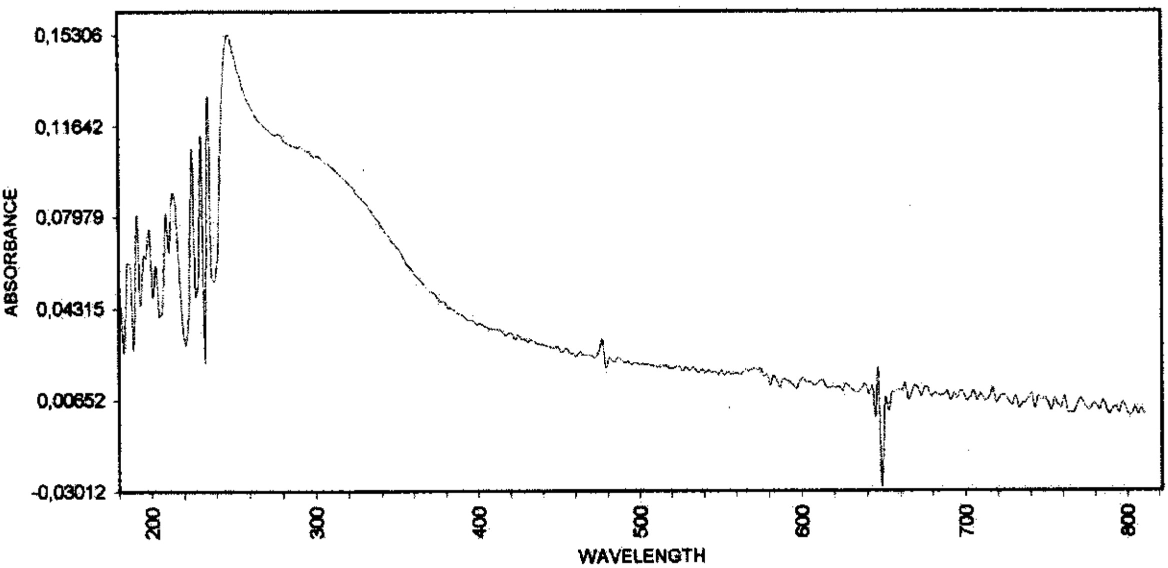

Fig.5: Absorbance of Distilled Water Passed Through Carbon-lime Bed

Absorbance of the individual filtrate samples was equal to (after 7 litres of filtrate have passed through the bed):

- Vc/Vca=0,375 mean absorbance value was A = 0,03
- Vc/Vca=0,50 mean absorbance value was A = 0,035
- Vc/Vca=0,625meanabsorbancevaluewasA=0,04

On the basis of results presented in Table 2 for the individual compositions of bed tested within the range Vc/Vc_a = 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 Vc/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 Vc/V_{Ca} in bed on effectiveness of purification is illustrated by absorbance of purified sewage samples for: Vc/V_{Ca} = 0,375 A = 0,03; Vc/V_{Ca} = 0,50 A = 0,035; Vc/V_{Ca} = 0,625 A = 0,04.

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

References

87-354318 T50 * SU 1308582: 1985, Removal of oily products and surface-active agents from sewages by electro-flotation method. Gieredment Res Inst, 85. 04. 19., SU 905041

89- 206032 T28 * US 4836921, 1989, Compact portable device for treatment of sewage containing oil or coolant. 89. 01. 30., US 008854

89-287800 T40 * HU T049091, 1987, Treatment of sewages containing organic substances by addition of cement, aluminum sulfate, sodium acrylane, iron sulfate-chloride and yeasts. TOROK G., 87. 02. 19., HU 000632.

89-345240 T47 * IO 1258799, 1988, Organic sewage treatment by addition of calcium ions, nitrification, denitrification, addition of iron ions and so on. EBARA INFILCO KK, EBARA SOGO KENKYUSHO KK, 88. 04. 06., JP 083020.

Aurelle, Y., A. Abadie and H. Roques; 1973. Traitment par coalescence sur resins oleophiles des eaux residuaires contenant des hydrocarbures emulsionnes., C.B.E.D.E., 3,352,108.

Aurelle, Y., H. Baumann, J. Bonet, P. Masse and A. Verdier; 1978. Traitment des huile solubles par les polyelectrolytes., La Technique de L'eau de L'assainissement, 394, Bruksela.

Bal, S., M. Grzechnik, A. Koszyk and C. Olczak; 1988. Method of coke sewage treatment. Polish patent 145282,88.12.31.

Bartkiewicz, B., 1974. Purification of sewages containing used emulsion coolants. Scientific Papers, Politechnical Publishers, Warsaw. 29,74.

Bartkiewicz, B., 1976. Studies on application of electroflotation for purification of sewages containing oil emulsions. GW and TS, 8,227.

Bodzek, M., O. Kominek and J. Zieliński; 1981. Application of reverse osmosis and ultrafiltration in technology of water and sewages. New Technique in Sanitary Eng. 13, Water supply and sewage Sys., "Arkady" Publishers, Warsaw.

Bukowski, A. and E. Grudzińska; 1975. Studies on application of polypropylene wastes for sewage treatment. GWiTS v.11.345 16.

Chojnacki, A. and B. Bartkiewicz; 1972. Problem of oils and surface active agents removal on the example of sewages containing emulsions. GW I TS, 8.

Chojnacki, A., 1965. Technology of industrial sewages. PWN Łódź - Warsaw

Dakovic, S., 1985. Fette, Seifen, Anstrichm., 87,11.

Humenick, M.J. and B. J. Bavis; 1978. High rate filtration of refinery oily wastewater. JWPC, 8.

Koziorowski, B., 1980. Treatment of industrial sewages. Scientific Technical Publishers, Warsaw.

Lendzion, P., A. Słodwiński, B. Zawadzki, J. Frąckowiak and P. Wojciechowski; 1999. Purification of industrial sewages containing considerable amounts of oil. Polish patent 286955, 90. 09. 18.

Lindh, L. and J. Dahlen; 1989. J. Am. Oil Chem. Soc., 66,972.

Małaczyński, M., 1979. Technique of protection against pollution by ships. Marine Publishers. Gdańsk.

Mańczak, H., 1972. Technical basis of water protection against pollution. Politech. Publishers. Wrocław., Wrocław.

Mayo, F., 1960. Deoling with pollution on water on shores. Institute of Petroleum Meeting, Brighton.

Meibaum, Z. and Z. Stasch; 1978. Removal of emulsified oils from sewage by electrocoagulation method. Chem. Industry, 8,407.

Meinck, F., H. Stoof and H. Kohlschutter; 1975. Industrial sewages. „Arkady" Publishers, Warsaw.

Pysiak, J., B. Tymiński, P. Stefaniak, P. Turowski, W. Rędziński and L. Szalkowski; 1992. Method of purification of water polluted with petroleum products and mechanical suspension. Polish patent 155134, 92. 04. 30.

Strzelczyk, A., 1974. Filtration with supportive filtration agents. Fuel and Energy Management, 5.

Urbański, G., 1981. Elektrochemical pollution of sewages containing oils. Proceedings of II-nd Conference, Kraków 351-367.