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Adsorption Method of Emulsion Coolants Separation Part II. Studies on Effectiveness of Sewage Purification on Regenerated Carbon – Lime Bed

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Abstract: The effectiveness of oil sewage purification by filtration on a new-prepared carbon-lime bed at the voluminal ratio of carbon ash to waste lime was equal to V_c/V_{Ca} = 0,5 and moreover, on the same bed saturated with oil wastes and then regenerated. The ether extract, COD, absorbance and inorganic contaminations with components of bed such as Ca^{+2}, Cl^- were determined. The effectiveness of sewage purification pn regenerated bed and permeability of the bed after regeneration are similar to those for new-prepared bed.

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

Introduction

Decreasing resources of pure water as well as progressing degradation of natural environment by various wastes and particularly by industrial sewage contaminated with oil cause serious damage to people and nature.

Solubility of oil in water is very low i.e. only several mg/dm^3. The emulsified oils form hydrophilic oil emulsions i.e. oil in water or hydrophobic ones i.e. water in oil (Gilewicz, 1974 and Koziorowski, 1980). The sewages particularly difficult for purification are oil emulsions obtained by mineral oils mixing with water which are applied mainly in engineering, metallurgical and automotive industries as coolants during machining and plastic forming. Formation of stable emulsions is preceded by surface tension decrease on the phase boundary by surface-active agents consisted of hydrophilic part eg. ($-SO_3Na$) and hydrophobic one eg. hydrocarbon chain ($CH_3(CH_2)_n-$). Many chemical, thermal, physicochemical, biological and electrical methods are applied for destabilization of the stable oil emulsions (Aurelle *et al.*, 1973; Aurelle *et al.*, 1978; Bartkiewicz, 1974; Bartkiewicz, 1976; Chojnacki and Bartkiewicz, 1972; Chojnacki, 1965; Humenick and Bavis, 1978; Lindh and Dahlen, 1989; Małaczyński, 1979; Mańczak, 1972; Mayo, 1960; Meibaum and Stasch, 1978; Meinck *et al.*, 1975; Strzelczyk, 1974; Urbański, 1981).

The physicochemical treatment based on coagulation, filtration, ultrafiltration, sorption, coalescence and reverse osmosis are the most often applied methods for destabilization of stable oil emulsions in sewages (SU, 1989; FR, 1988; DD, 1988; Bodzek *et al.*, 1981; Hupka and Gutkowski, 1988; Hupka *et al.*, 1990; Koziorowski, 1980; Meinck *et al.*, 1975; Solecki and Stopa, 1992)

One of the most important methods commonly applied consists in sewage deoiling by sorption on the surface of solid where both coagulation and coalescence of the oil molecules can be ·nvolved. The hydrophobic substances (oilphilic), mentioned below, are applied as sorbents.

- sorbents of natural origin such as chalk, talk, bentonite, peat, straw, cork (DE, 1988; Bukowski and Grudzińska, 1975; Humenick and Bavis, 1978; Hupka *et al.*, 1980; Kobierski and Stężała, 1991; Moore *et al.*, 1978; Pietraszak, 1988; Strzelczyk, 1974)
- synthetic sorbents such as resins (SU, 1984), polypropylene wastes (Mayo, 1960), plastic foams (Bortel and Wyroba, 1973; Mayo, 1960; Turbeville, 1973) and mixed eg. cement, sand and chalk (JG, 1987; DE, 1988; US, 1988; Solecki and Stopa 1992).

An important feature of each adsorbent is its sorption capacity. Complete saturation i.e. sorption capacity is determined by quantity of oil absorbed by adsorbent mass or volume. Sorption capacities of the selected sorbents occurring in water-oil mixture in turbulent motion are presented below:

Sorbent	sorption capacity [g oil/g adsorbent]
active carbon	0,15-0,22
viscose fibre	0,2-2,6
tyre cord	4,5-7,5
urea-formaldehyde resins	12-40
flexible polyurethane foam	25-63

The sewage purification by adsorption on beds is an unsatisfactory solution from the environment protection point of view for the reason that the impurities are transported from the liquid to solid phase and the heaps with used oiled adsorbent are formed what in consequence also leads to environment pollution. Therefore, the used oiled adsorbents must be regenerated and then reused in adsorption process.

In the first part of our studies (Sobczak *et al.*, 2002), the results of sewages (water-oil emulsions) purification by adsorption on carbon ash-waste lime bed were presented. In the present studies, the used bed was subjected to regeneration and the effectiveness of sewage purification on the regenerated carbon-lime bed was determined.

Materials and Methods

Regeneration of the bed and repeated studies of adsorption were carried out for carbon ash-waste lime voluminal ratio V_c/V_{Ca} = 0,50. The bed was regenerated by bringing it into the fluidal state by means of hot water (t=95°C) and organic impurities as well as a part of intergrain "carbon-lime powder" were removed. After regeneration, the height of bed was reduced by approx. 13%.

The experiments were carried out in the column (ID = 50 mm, height L_0 = 700 mm) with porous bottom; the bed height in column was L = 640 mm. The stream of emulsion flowing in was equal to the stream of filtrate flowing out. The emulsion level was kept at the height of regenerated bed (H = L). Permeability of bed k = u (Sobczak *et al.,* 2002) was determined from the formula:

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

The granulated waste lime in composition with carbon ash was applied for adsorption; its composition was presented in (Sobczak *et al.,* 2002) and the voluminal ratio of ash to lime was V_C/V_{Ca} = 0,5.

The studies on the effectiveness of purification on the newly prepared bed were carried out till the bed was saturated (V_{sewage}= 7 dm^3 was accepted) and then the bed was regenerated and the studies were repeated on regenerated and completed bed.

The used oil emulsion – VECO EMULEX ES-12 and water in voluminal ratio of 1:30 (Sobczak *et al.,* 2002) were applied for the studies on the effectiveness of emulsion separation.

The effectiveness of sewage purification was determined on the basis of:

- content of substances extracted by petroleum benzine, [mg/dm^3]
- acidity of coolant and alkalinity of purified sewage [mmole/dm^3]
- Chemical Oxygen Demand (COD), [mg O_2/dm^3]
- absorbance of purified and raw (emulsion) sewage and distilled water filtered through carbon-lime bed
- content of calcium and chloride ions in purified sewage filtered by bed being composition of carbon ash and waste lime [mmole/dm^3].

Results and Discussion

Results of studies on sewage purification on newly prepared carbon-lime bed for V_C/V_{Ca} = 0,5 and on regenerated bed are presented in Tables 1-3 and in Figures 1-7.

Table 1: Results of Studies on Effectiveness of Emulsion Purification on the Bed Before Regeneration (voluminal ratio of carbon ash to waste lime V_C/V_{Ca} = 0,5)

No. of sample	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 [cm^3]	[m^3/m^2h]	[m^3/m^2h]	[ml] HCl	[mmole/ d m^3]	[ml] EDTA	[mmole/ dm^3]	[ml] $AgNO_3$	[mmole/ dm^3]	[mg/dm^3]	[mgO_2/ dm^3]
0	emulsion	-	-	-			-	-	-	-	8250,2	29700,7
1	purified sewage	1385	$2,39 \cdot 10^{-4}$	$2,39 \cdot 10^{-4}$	6,6	26,4	67,8	169,8	111,4	556,3	108,8	380,8
2	purified sewage	1726	$1,63 \cdot 10^{-4}$	$1,63 \cdot 10^{-4}$	7,5	30,0	41,8	104,7	70,0	348,5	102,2	378,1
3	purified sewage	2100	$1,04 \cdot 10^{-4}$	$1,04 \cdot 10^{-4}$	7,6	30,4	25,6	64,1	39,2	194,7	101,6	355,6
4	purified sewage	2730	$6,26 \cdot 10^{-5}$	$6,26 \cdot 10^{-5}$	8,2	32,8	18,8	47,1	23,0	113,8	73,2	285,5
5	purified sewage	5760	$1,44 \cdot 10^{-5}$	$1,44 \cdot 10^{-5}$	8,6	34,4	16,0	40,1	12,5	61,4	55,2	220,8
6	purified sewage	9500	$4,13 \cdot 10^{-6}$	$4,13 \cdot 10^{-6}$	9,7	38,8	12,8	32,1	9,9	48,4	46,8	159,12
7	purified sewage	14900	$2,12 \cdot 10^{-6}$	$2,12 \cdot 10^{-6}$	10,2	40,8	13,1	32,3	11,2	55,0	29,6	112,48

Table 2: Results of Studies on Effectiveness of Emulsion purification on the Bed after Regeneration (voluminal ratio of carbon ash to waste lime V_C/V_{Ca} = 0, 5)

No. of sample	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	COC
		s [cm^3]	[m^3/m^2h]	[m^3/m^2h]	[ml] HCl	[mmole/ dm^3]	[ml] EDTA	[mmole/ dm^3]	[ml] $AgNO_3$	[mmole/ dm^3]	[mg/ dm^3]	[mgO_2/dm^3]
0	emulsion	-	-	-	-	-	-	-	-	-	8250,2	29700,7
1	purified sewage	1680	$1,48 \cdot 10^{-4}$	$1,48 \cdot 10^{-4}$	9,2	36,8	43,0	107,7	44,2	219,7	124,8	474,2
2	purified sewage	2019	$1,12 \cdot 10^{-4}$	$1,12 \cdot 10^{-4}$	10,0	40,0	32,6	81,7	41,8	207,7	120,1	432,4
3	purified sewage	2355	$8,80 \cdot 10^{-5}$	$8,80 \cdot 10^{-5}$	10,2	40,8	28,0	70,1	32,6	161,8	89,5	313,3
4	purified sewage	2980	$6,87 \cdot 10^{-5}$	$6,87 \cdot 10^{-5}$	10,3	41,2	23,0	57,6	23,2	114,8	86,4	311,0
5	purified sewage	3300	$4,51 \cdot 10^{-5}$	$4,51 \cdot 10^{-5}$	10,6	42,4	17,5	43,8	15,8	77,9	59,2	224,9
6	purified sewage	3720	$3,31 \cdot 10^{-5}$	$3,31 \cdot 10^{-5}$	10,8	43,2	15,2	38,1	10,6	51,9	53,1	212,4
7	purified sewage	5160	$1,81 \cdot 10^{-5}$	$1,81 \cdot 10^{-5}$	11,2	44,8	12,8	32,1	7,2	35,0	38,2	148,9

Table 3: Comparison of Effectiveness of the Oil Sewage Purification on the New and Regenerated Bed

Voluminal Ratio of Bed Vc/Vc_a=0,50	Filtration Rate m^3/m^2h	C_{OH^-} mmol/dm³	C_{Ca+2} mmol/dm³	C_{Cl^-} mmol/dm³	Ether Extract mg/dm³	COD mg/dm³
New Bed	$4,13*10^{-6}$- $2,39*10^{-4}$	26,4 – 40,8	32,1 – 169,8	48,4 – 556,3	29,6 – 108,8	112,48 – 380,8
Regenerated Bed	$8,8*10^{-5}$- $1,12*10^{-4}$	36,8 – 44,8	32,1-107,7	35,0 – 219,7	38,2 – 124,8	148,9 – 474,2

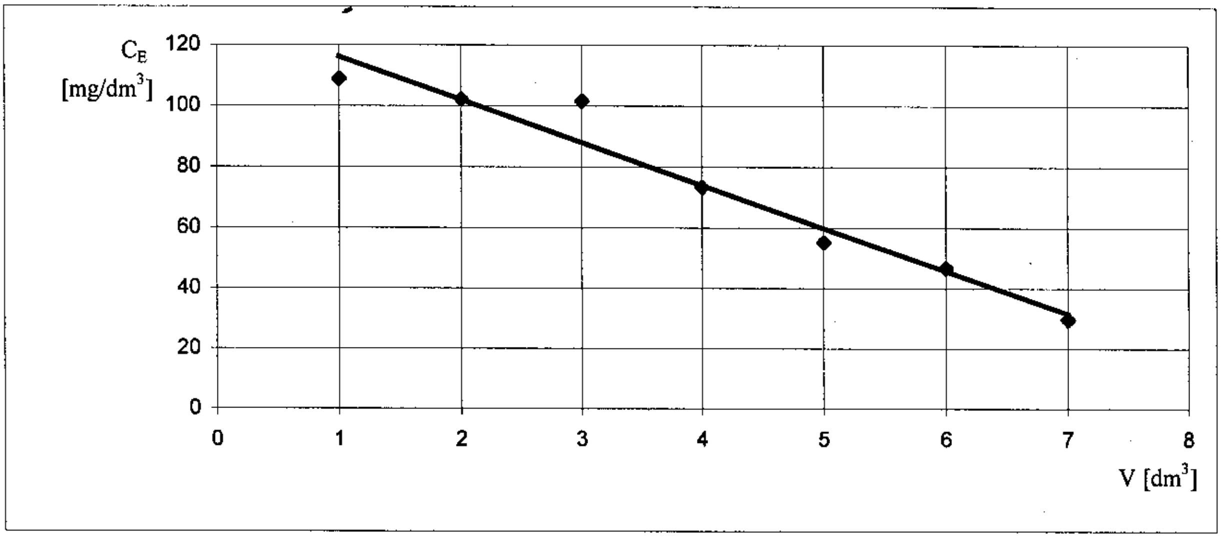

Fig. 1: Dependence Between Content of Organic Substances (ether extract) and Quantity of Sewage Purified on Carbon-lime Bed Vc/Vc_a = 0,50

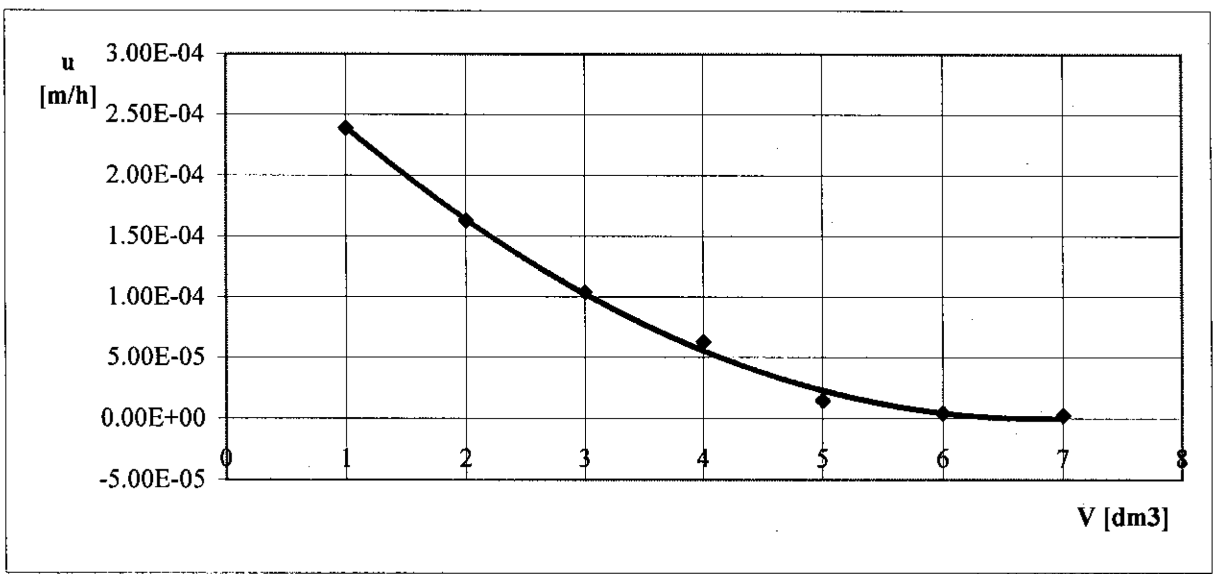

Fig. 2: Dependence Between Filtration Rate and Quantity of Sewage Purified on Carbon-lime Vc/Vc_a = 0, 50

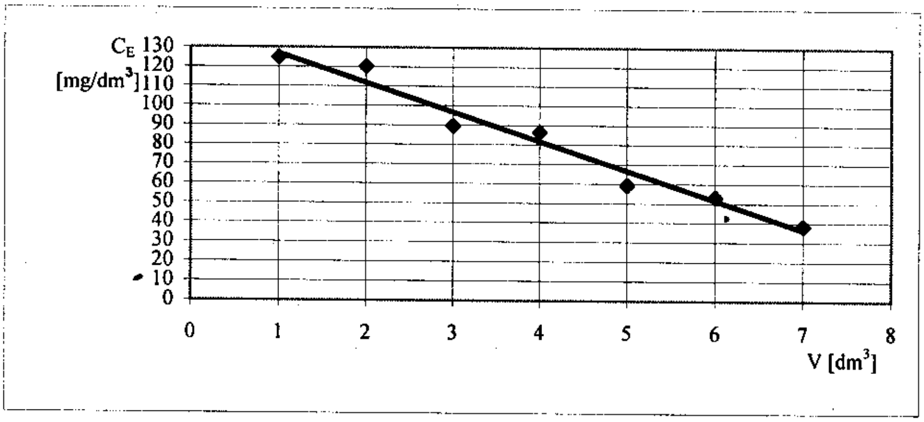

Fig. 3: Dependence Between Content of Organic Substances (ether extract) and Quantity of Sewage Purified on Regenerated Carbon-lime Bed $Vc/Vc_a = 0{,}50$

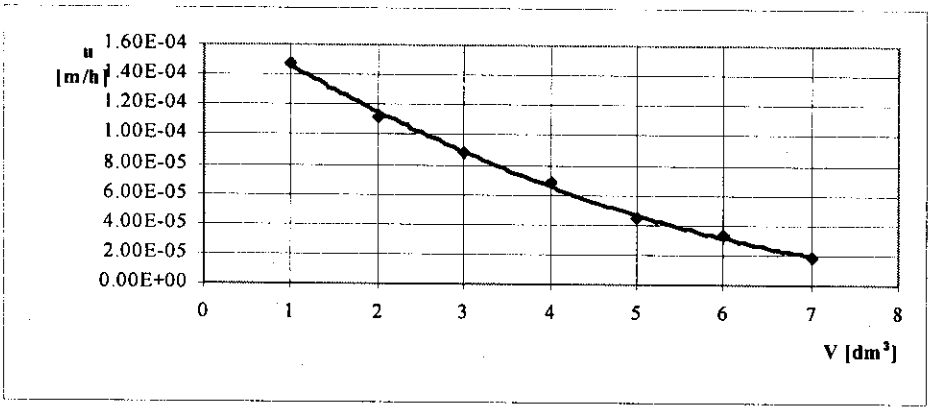

Fig. 4: Dependence Between Filtration Rate and Quantity of Sewage Purified on Regenerated Carbon-lime $Vc/Vc_a = 0{,}50$

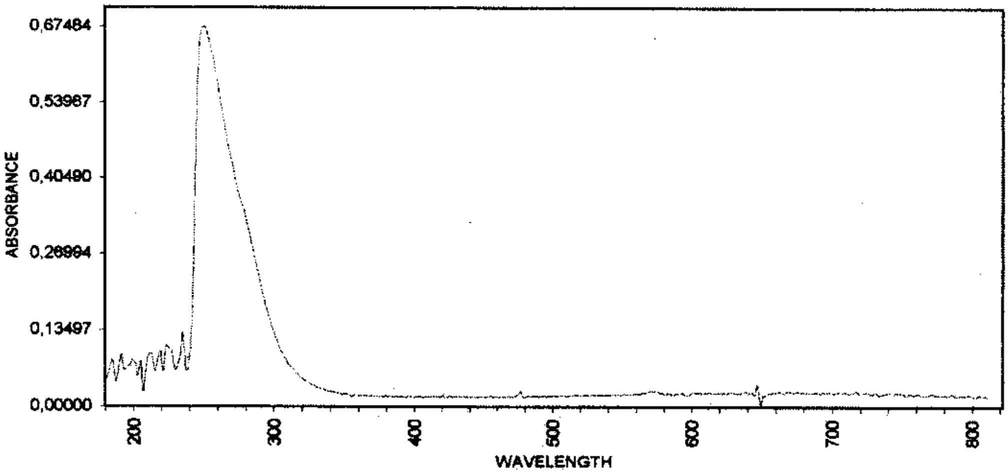

Fig. 5: Absorbance of Sewage Purified on Carbon-lime Bed $Vc/Vc_a = 0,\ 50$ before Regeneration

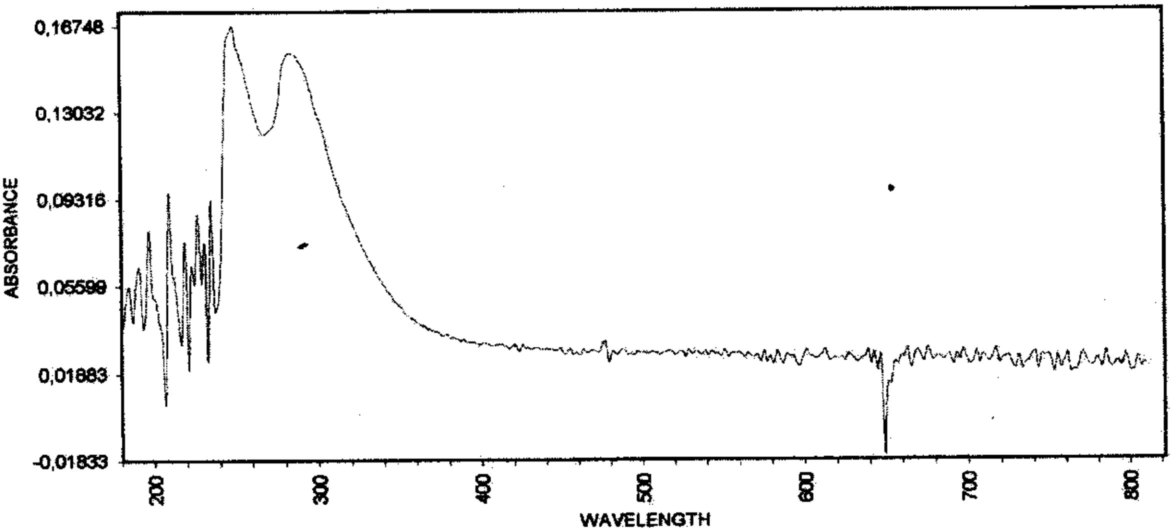

Fig. 6: Absorbance of Sewage Purified on Carbon-Lime Bed Vc/Vc_a = 0, 50 after Regeneration

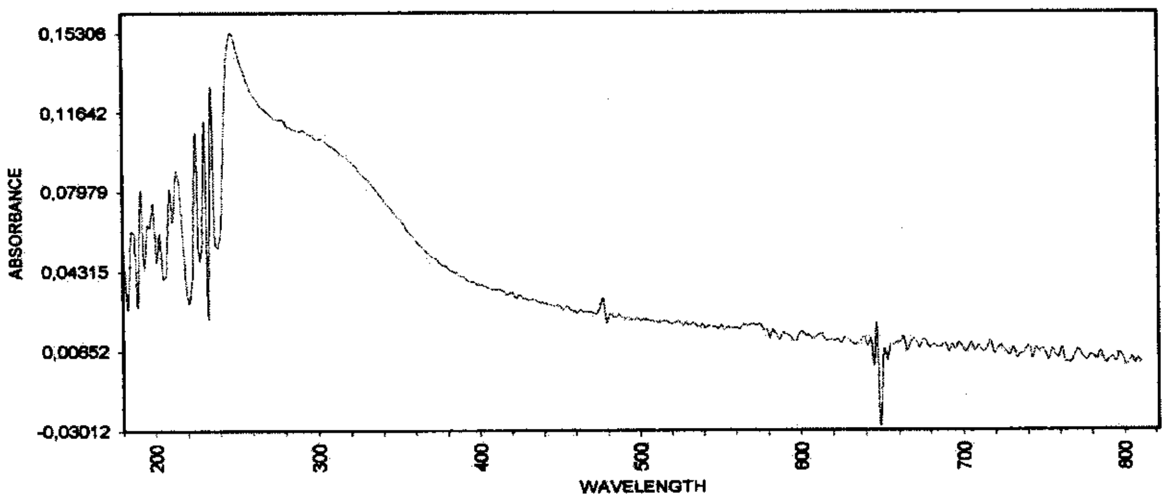

Fig. 7: Absorbance of Distilled Water

The results obtained for experiments carried out for the bed before and after regeneration (Vc/Vc_a = 0,50) and presented in Tables 1-3 and in figures show that:

- the bed after regeneration is characterized by the permeability and effectiveness of sewage purification similar to that of newly prepared bed
- during sewage filtration on newly prepared and regenerated beds the similar degrees of sewage purification were achieved, however filtration rate in the case of regenerated bed was slightly higher, what could result from the fact that even the smallest grains were removed during regeneration while the bed was brought into fluidal state by means of hot water
- during filtration on a new and regenerated beds the decrease in quantity of substances extracted by ether and reduction of flow rate (caused mainly by disintegration of granules to small molecules and by clogging the intergrain canals with adsorbed oil) are observed as the amount of sewage passed through the bed is higher,
- absorbance values (being the measure of degree of sewage purification) measured for the samples of sewage purified on newly prepared and regenerated beds were similar
- the similar absorbance values for purified sewage and distilled water passed through carbon-lime bed prove about high degree of sewage purification.

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