

PURIFICATION OF WASTE WATER FROM COKING AND
COAL GASIFICATION PLANTS USING ACTIVATED CARBON

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I. Introduction

Under environmental aspects the purification of waste water containing organic substances becomes more and more important. It is known that the conventional processes, especially biological techniques, are not able to remove all organic compounds out of the wastes. These resistant compounds inhibit, especially if they are toxic, the biological process of cleaning. So they accumulate in the effluent water causing a pollution increase of our streams, lakes, and seas.

In recent times different methods are discussed to solve this problem, e.g. reverse osmosis, precipitation by special agents, the burning of high concentrated wastes, and the adsorption on suitable adsorbents.

Under the industrial wastes the phenolics from coking and other coal-using plants are most undesirable. They contain some compounds in such a high concentration that they are particularly noxious. The concentration range of some compounds contained in waste water from coking plants is listed in table I. Depending on the special kind of treatment systems of coke oven gas there are two or three types of waste water: the condensate, the ammoniacal liquor, and the decanter waste water. We consider now only the condensate and the waste water after the ammonia decanter. Fig. 1 shows a simplified scheme of a treatment system of coke oven gas. The water coming from the tar separator is called condensate, and after decanting the uncombined ammonia decanter waste water.

The main methods to clean this waste water are:

- extraction by benzene or isopropylether
- biological treatment
- adsorption on activated carbon

One of these techniques, the adsorption, is indicated in fig. 1 as a possible step of waste treatment to get clean water.

The extraction needs further steps of purification because the removal of organic carbon by this process reaches only about 55 %.

The biological treatment is loaded with many difficulties.

Some of them will be discussed herein short. As table II shows there are some compounds, e.g. benzene, naphthalene, anthracene, HCN, that cause a high value of TOC or COD, but the BOD-value is zero, that means these compounds are not decomposable by microbes. Thereby differences can be caused in the valuation of the grade of purification. Up to now in the BRD the quality of effluents are often measured by BOD- and COD_{Mn}-values. But as to be seen in table II a low BOD-value of a

treated waste is no guaranty for sufficiently cleaned water. On the other side many of the inorganic salts or ions cause a high COD_{Mn} value, that cannot be reduced by biological decomposition.

Moreover, the operation of a biotreatment plant is very complicated. Particular conditions are to be adhered to, to enable a high efficiency of the purification process. The limiting values of some contraries to the three main decomposing compounds of coking plant effluents are set out in table III. It shows that these compounds exercise a strong influence of the decomposition of each other.

The adsorption on activated carbon nowadays often used in advanced treatment systems for reclamation of drinking water can help to solve the problems of purification of high concentrated industrial effluents like phenolic wastes. In the following it shall be pointed out, which parameters lead to the design of an adsorption plant and how it works.

II. Determination of design parameters

The use of activated carbon for industrial wastes postulates special characteristics of the carbon and the process of adsorption and reactivation. The carbon must have a high internal surface area per unit volume and special adsorption affinity to the waste water compounds, furthermore, from the economic point of view an extreme hardness and low reactivity of the carbon is important to make its reactivation and reuse possible. The design of the adsorption unit and the operation of the adsorption process must allow the best use of the adsorption capacity of the carbon to minimize the cycling amount of activated carbon. The reactivation of the charged carbon has to be performed at such carefully controlled conditions that the adsorption capacity of the carbon is fully regained and the carbon loss is at a minimum. Bergbau-Forschung has developed a process of waste water treatment by activated carbon that combines these requirements. To determine the design parameters of such an integrated adsorption/activation plant we use a serie of tests that will be discussed now in brief.

II.1 Adsorption isotherms

Knowing the waste water analysis and the desired quality of the effluent, adsorption isotherms would be run on various representative samples to determine the feasibility of using activated carbon to remove the organics from this waste and to find the most suitable carbon as well as its grain size for the sorbable components. This test consists of contacting a fixed quantity of waste with varying amounts of carbon for a given time. The amount of organic removal at the varying dosages is determined by TOC-measurement and gives an indication of the amount of carbon required to treat this particular waste.

II.2 Column test

With the knowledge of kind and grain size of activated carbon the next test is to be run. The waste water at a constant but in several runs varying flow-rate passes through a carbon column of a suitable length and diameter which depends on the used grain size. By measuring the concentration of sorbable compounds in several heights of layer as a function of time or throughput the so-called curve of breakthrough can be achieved by equation 1.

$$\frac{c}{c_0} = f(\text{time}) \quad 1)$$

Using the mass-transfer-zone concept it is possible to determine from these curves the essential parameters for design as it is shown in the scheme of fig. 2. At first the velocity of the mass-transfer-zone between the layer heights H_1 and H_2 has to be determined by equation 2.

$$v_F = \frac{H_2 - H_1}{t_{H_2} - t_{H_1}} \quad 2)$$

In the continuous process v_F is equivalent to the velocity of activated carbon \dot{V}_C circulating the adsorption/reactivation plant, calculated by equation 3.

$$\dot{V}_C = v_F \cdot A \quad A = \text{sectional adsorber area} \quad 3)$$

The width of the mass-transfer-zone H_{MTZ} , given by equation 4,

$$H_{MTZ} = v_F \cdot (t_2 - t_1) \quad 4)$$

depends on the slope of the breakthrough curve and gives the minimum height of the adsorption layer. In the ideal case v_F and H_{MTZ} are independent from the position of layer, and constant during the process of adsorption. A very important factor is the achieved adsorbate loading of the carbon layer, calculated by equation 5.

$$Q(t) = \frac{\dot{V}_w(t)}{M_C} \int_0^t (c_0 - c) dt \quad \begin{array}{l} \dot{V}_w(t) = \text{mass flow of waste} \\ \text{water} \\ M_C = \text{carbon amount in} \\ \text{adsorber} \end{array} \quad 5)$$

The higher the loading, the less carbon is required per unit volume of waste and consequently the less is the consumption of energy and carbon loss during reactivation.

To have an idea of the adsorption tests some isotherms are shown in fig. 3. The upper diagram on the left hand side shows isotherms of three types of activated carbon treated with the same waste. The slope of the curves and the values of charge indicate which of the three carbons are the most suitable ones for cleaning the special waste. To get the specific adsorption capacity per unit volume the values of adsorbate loading are to be multiplied by the bulk density of the carbon. The lower diagram shows isotherms of three different types of coking plant effluents treated with the same activated carbon. As to be seen the isotherms differ remarkably due to the different kind and content of compounds. On the right hand side in the upper diagram two adsorption isotherms are shown. They are determined by treatment of one carbon with condensate (curve 1) and decanter waste (curve 2) of the coking plant Kamp-Lintfort. Here the higher TOC-content causes a higher value of charging. In the lower diagram two curves are shown which are calculated from the breakthrough curves of pilot column tests. Although the TOC-contents of the wastes are equal to those from the curves in the upper diagram, the achieved values of charge on the same carbon are different. The effect can be explained by the different conditions of lab-scale test and pilot column test. In the lab test the isotherms are got at decreasing concentration, in the column test the carbon is treated at quasi-constant concentrations. As we have found out for different types of wastes with a complex mixture of compounds, differing in adsorption affinity to the carbon, in the first phase of adsorption

a higher loading is achieved at decreasing concentration. Later on it might happen that the higher concentration in the column test causes a higher adsorbate loading, but often the active centers of the carbon are blocked so that no increase in charge is possible.

Fig. 4 shows representative breakthrough curves measured in pilot column tests with decanter waste of a TOC-content of 1000 mg/l at a flow-rate of 10 m/h. The steep slope of the curves is brought about by the fast kinetics of adsorption standing out for the main compounds of the waste. Furthermore, the curves are parallel to each other showing a constant velocity of the mass-transfer-zone. Steep and parallel curves indicate a small zone of mass-transfer, that means the required height of carbon layer is low.

II.3 Regeneration test

Is the adsorption in general well understood, the thermal regeneration of the loaded carbon, although of great importance, has been not sufficiently investigated till now. Our investigations show that there are two steps: first the desorption of reversibly bonded compounds and second the reactivation with steam or similar gases to destroy those compounds that are irreversibly bonded or decomposed on the internal surface of the carbon during the heating phase. With a special arrangement of thermal-balance, gaschromatograph and mass-spectrometer, we have investigated the desorption process. Thereby it is not only possible to identify the adsorbed substances, we get also information about the quantity of desorbed products and the possibility of recovering valuable by-products from the waste. Furthermore, it can be checked in which position of the adsorber unit the single components of the waste are adsorbed.

Fig. 5 shows desorption curves of compounds out of different wastes. The curves in the lower diagram are gained from carbons loaded in decanter waste water with a TOC-content of 1000 mg/l, taken from a position of the column near the water inlet. The main substances are phenol, cresol, naphthalene and SO₂ from decomposition of sulphurous compounds. Is the carbon charged in the condensate after the tar separator the main substances are as shown in the upper diagram: phenol, cresol, naphthalene, but additional dimethylphenol and hydrocarbons C₃ and C₈.

Fig. 6 shows desorption curves from carbon samples in different positions of a column treated with decanter waste. The carbon of the adsorber outlet is mainly charged with phenol and sulphurous compounds. In the middle of the column also cresol is adsorbed, and in the first layer of carbon at the column inlet naphthalene is predominantly adsorbed. From this experiments one can get a concentration profile of adsorbed substances over the length of the carbon column, as shown in fig. 7.

The simultaneous processes of desorption and reactivation are studied in lab-scale fluidized bed which was operated batchwise. With this set-up the conditions for the regeneration of loaded carbons are experimentally determined. After the column test the charged carbon is regenerated in this fluidized bed by varying temperature, residence time, and partial pressure of steam or other reactive gases. By measuring the adsorption activity and the carbon loss of the reactivated carbon the conditions for regeneration are optimized. These data and the amount of circulating carbon lead to the design of the reactivation unit.

III. Pilot plant

With the data obtained in the above described tests it is possible, on principle, to design an integrated adsorption/reactivation plant. But for commercial purposes it is necessary to run tests for some time with a pilot column at the waste producing plant, because the operational wastes can strongly change in amount and concentration due to the rhythm of production.

Bergbau-Forschung, as a research institute of the mining companies of Western Germany, has investigated with priority the waste water from coking plants. A pilot adsorption plant with a maximum throughput of 300 l/h was in operation for two years, and some of the results shall now be pointed out. The flow scheme of the pilot adsorption plant is shown in fig. 8. A side stream of decanter waste water is pumped to a water receiver through a prefilter, to remove the mechanical impurities. From this the waste water flows from bottom to top through the adsorption columns. The discharge of the adsorbent can take place through a special outlet mechanism during operation. The filling-up of the carbon is carried out hydraulically by water from the receiver. The flow-rate through the adsorber was changed between 1 and 20 m/h. To have the possibility of measuring the breakthrough of the mass-transfer-zone in different heights the carbon column has a length of 5 m and the TOC-content as a function of layer height was continuously recorded. The typical curves of breakthrough, measured in this pilot columns, are already shown in fig. 4. To get a sufficiently cleaned water the TOC-measurement in the layer height of 2.50 m was taken as setting-means for carbon discharge. A reaching of breakthrough of 95 % input-concentration at this position led to the discharge of this completely loaded carbon layer during operation, and the filling-up of the 2.50 m column with fresh resp. reactivated carbon.

Fig. 9 presents the data of TOC-removal over an operation time of 10 months. As to be seen the input TOC ranges between 800 and 1900 mg/l, the output between 80 and 250 mg/l. It was possible to show that the output TOC was caused by cyanides and thiocyanates. The loaded carbon was reactivated in a reactivation pilot plant on the Bergbau-Forschung area. From fig. 9 it can be seen that in the ten months of operation the whole adsorber filling was reactivated 29 times.

A more detailed information gives fig. 10. Here the TOC and BOD-content is plotted against the operation time. As to be seen the removal of COD is different from that of TOC. The percentage removal ranges for TOC between 90 and 95 % and for BOD between 82 and 99 %. For these tests we used different activated carbon with the same grain size of 2 mm and different flow rates to determine their influence on the important parameters like width, H_{MTZ} , and velocity, v_F , of the mass-transfer-zone, and the loading of the used carbon. In fig. 11 H_{MTZ} is plotted as a function of flow rate and bulk density. Within the range from 340 to 500 g/l bulk density has no remarkable influence, but a change in the flow rate from 5 to 20 m/h doubles the value of H_{MTZ} .

In a similar way the velocity of the mass-transfer-zone v_F is influenced by bulk density and flow rate as shown in fig. 12. The achievable charge of the carbon does not appreciably depend on bulk density, flow rate, and concentration as shown in fig. 13.

The success of reactivation is shown in fig. 14. It was possible to operate at such conditions that the adsorption activity, set forth for loading and HMTZ, could always be regained for any number of adsorption/reativation cycles. For the operation costs the knowledge of the carbon loss is very important. Fig. 15 shows that after a first period of different conditions in the reactivation unit the carbon loss got into its stride of 2 to 2.5 %. During the two years of pilot plant operation we got the average values of removal of the main impurities of the waste listed in table IV.

Impurities	Content (mg/l)	Removal (%)
phenols	650 - 1400	> 99
cyanide	5 - 35	45 - 70
thiocyanate	120 - 450	30 - 80
iron	40 - 150	30
solids	300 - 3000	> 99
TOC	800 - 2000	85 - 95
COD _{Mn}	2000 - 4000	80 - 99

Table IV: Content of main impurities in decanter waste and its removal by adsorption

IV. Demonstration plant

The good results of pilot plant operation gave rise to plan a demonstration plant with a throughput of 25 m³/h, that is the effluent of a medium sized coking plant. Table V gives the essential design data obtained from pilot plant results. Fig. 16 shows a scheme of the projected plant. From a tank 1 the waste water is pumped through a two-stage prefilter, then uniformly distributed by a suitable system over the cross section of the adsorber flowing from the bottom to the top where it leaves the adsorber sufficiently cleaned. The distribution system allows also a plane parallel discharge of the charged activated carbon. With an air-lift pump 5 the carbon is transported up to a dewatering screen 6 and then dosed with a feeding-screw 9 into the reactivation unit 10. The reactivated carbon is completely wetted in the quench tank 11 and then fed back into the adsorber. The detail engineering of this plant has begun, and we hope that it will be under construction by the end of the year.

tion/regeneration plant

4. regeneration of the carbon allows its reuse for many cycles
5. a very small floor space required.

These advantages result in the fact that adsorption on activated carbon is a suitable process for the purification of concentrated industrial wastes.

Table I: Composition of waste water from coking plants

compounds	condensate (mg/l)	ammoniacal liquor (mg/l)	decanter waste water (mg/l)
NH ₃ (total)	6000 - 8000	8500 - 15000	20 - 4500
NH ₃ (uncombined)	2000 - 6000	8000 - 12000	20 - 1000
CO ₂	2400 - 3900	3000 - 14000	-
H ₂ S	300 - 900	1000 - 5000	2 - 50
HCN	55	200 - 2000	0 - 20
HCNS	50	700 - 1200	0 - 800
phenols	700 - 3200	2000 - 3000	50 - 2500
pyridinebases	200 - 500	100 - 200	-
fix. acids		3400 - 5600	20 - 600
pH-value	8,0 - 9,0	9,0 - 9,5	5,0 - 11,5

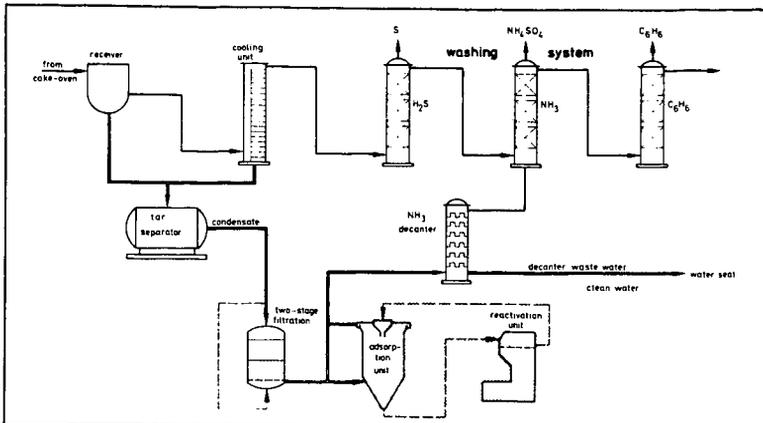
Table II: Characterising values of compounds from coking plant effluents

compound in solution (100 mg/l)	TOC (mg/l)	COD _{Mn} (mg/l)	BOD ₅ (mg/l)
NaCl	0	3,3	-
NH ₄ Cl	0	9,1	-
Na ₂ CO ₃	11,3	1,8	-
NH ₄ SCN	15,8	64	-
H ₂ S	0	190	187
HCN	70,5	0,2	0
phenol	76,6	238	178
o-cresol	77,7	173	164
m-cresol	77,7	172	170
pyridine	75,7	0,6	115
benzene	92,5	0,8	0
naphthalene	93,6	23,4	0
anthracene	94,5	16,2	0
Cl-ion	0	5,5	-
SCN-ion	20,7	77,6	-
SO ₃ -ion	0	19,7	-

Table III: Limiting values for biological treatment of coking plant effluents

temperature: 25 - 35 °C
 pH-value: 6,5 - 8,0
 phenol-content: < 500 mg/l

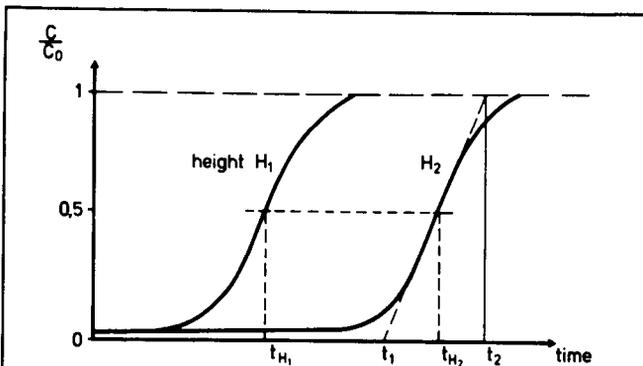
compounds to decompose	contraries	limiting values (mg/l)
phenols	ammonium	1700
	thiocyanate	250
	sulphide	25
	metal-ions	5
thiocyanate	ammoniumchloride	1000
	thiosulphate	100
	phenols	25
	metal-ions	5
ammonia	phenols	50
	thiocyanate	10
	cyanide	10



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Fig. 1: Treatment system of coke oven gas
- simplified scheme -

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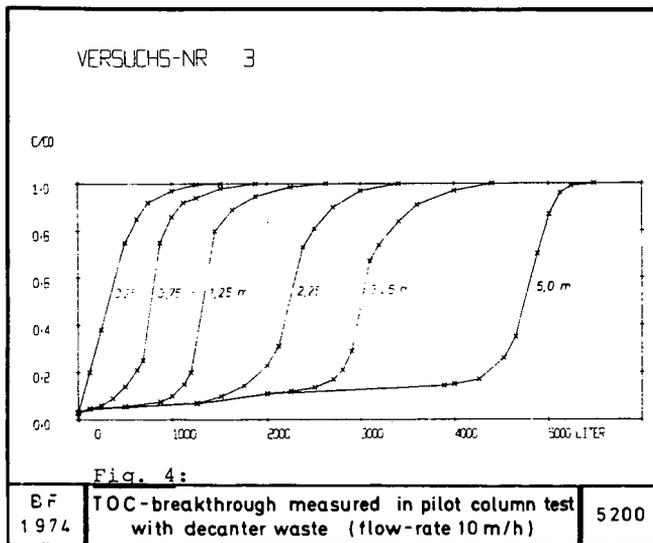
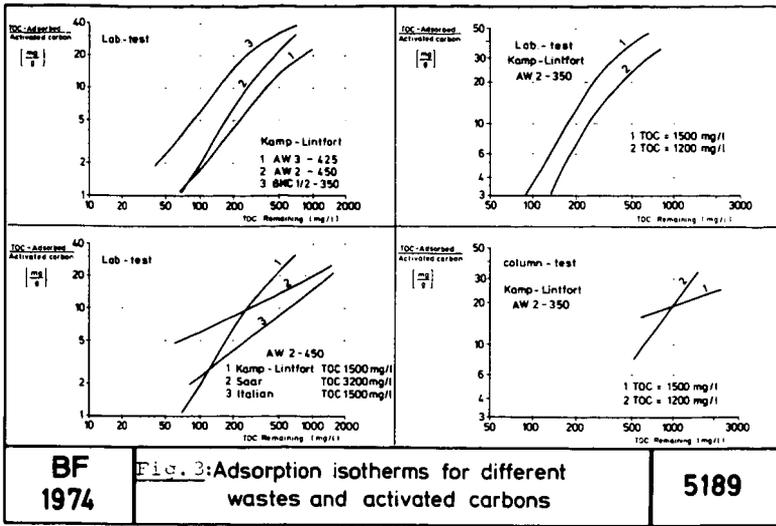


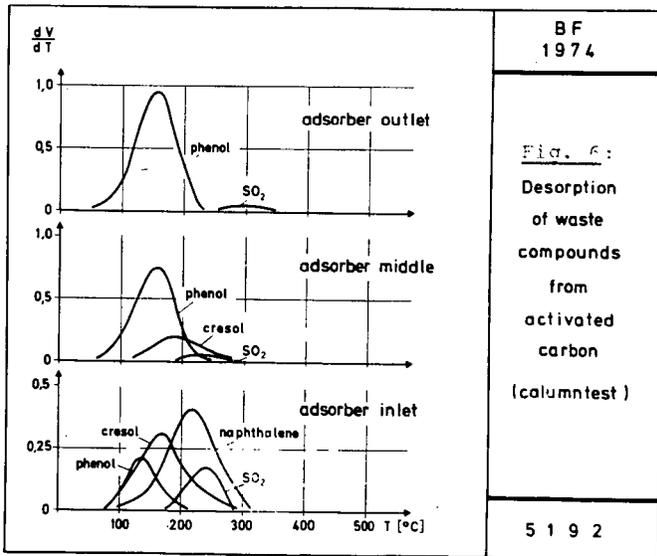
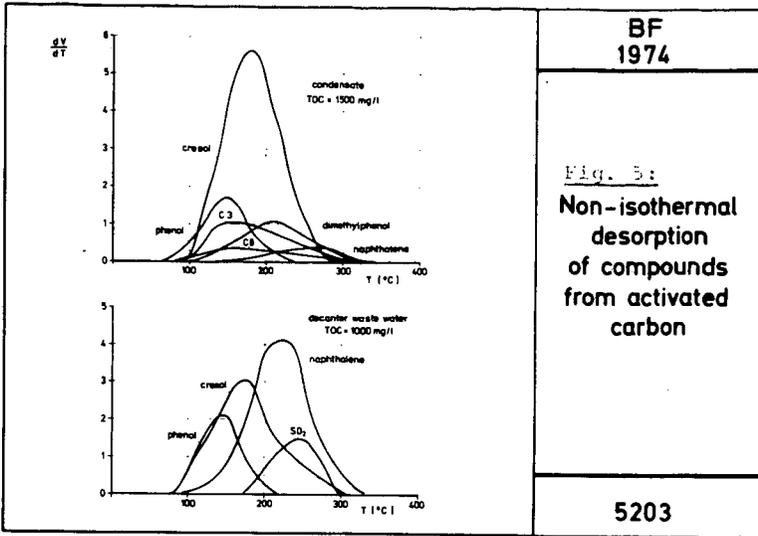
(1) $\frac{C}{C_0} = F(t)$ (3) $\psi_c = \psi \cdot A \left[\frac{m^2}{h} \right]$ (5) $Q(t) = \frac{V_M(t)}{M_C} \int_0^1 (C_0 - C) dt$
 (2) $\psi = \frac{H_2 - H_1}{t_{H_2} - t_{H_1}} \left[\frac{m}{h} \right]$ (4) $N_{MTZ} = \psi \cdot (t_2 - t_1) [m]$ (5a) $Q(t) = \frac{V_M}{\psi} \cdot (C_0 - C) \left[\frac{Q}{t} \right]$

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Fig. 2:
Mass-transfer-zone concept for
determining process parameters

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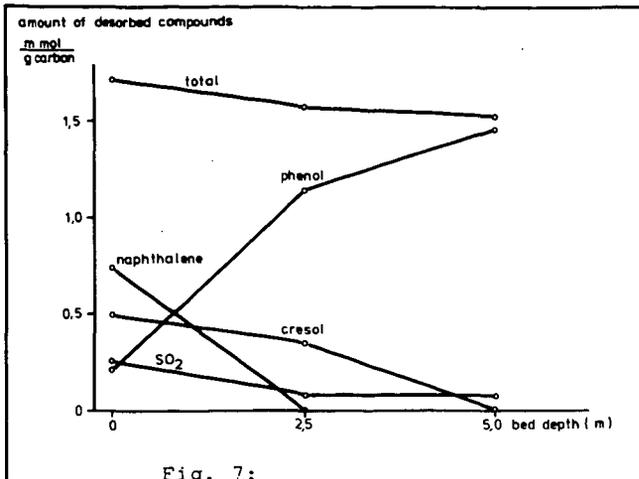
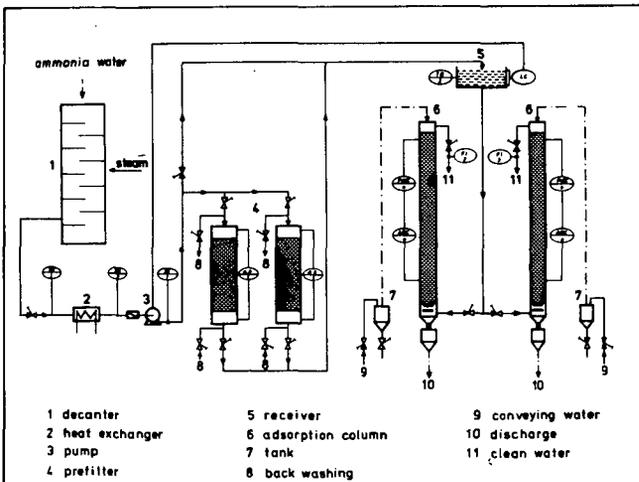


Fig. 7:

BF 1974	Desorption of compounds from activated carbon (column test)	5191
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BF 1974	Purification of coking plant effluents Fig. 8: -pilot plants flow sheet-	5190
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