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USE OF SORPTIVE FILTERS IN THE REMOVAL OF REFRACTION COMPOUNDS FROM SOME BIOLOGICALLY TREATED INDUSTRIAL WASTES

Laboratory research work was carried out to compare filtration efficiency of sorptive filters both with constant and moving beds. Testing the artificially prepared phenol wastewater and coke wastewater, it was indicated that the LUB is to be found in the sorptive filter with constant bed. In general, that area depends, among other things, on coke grade, type of wastewater, height of filter bed, filtration velocity and purfication grade of treated wastewater.

In filter with moving bed, the sorbent capacity is fully utilized, and sorbed load in disconnected segment is a balance load under the specified filter conditions. Therefore, sorptive filters with moving beds prove to be more efficient than filters with constant beds, the more so as it is possible to install carbon regeneration equipment to get closed recirculation of activated carbon.

1. INTRODUCTION

Some treated industrial wastes show unsatisfactory quality even after multiple stages of treatment, with biodegradation as the last stage in most cases. For example treated industrial wastes from solid fuel treatment and pulp-mill liquors retain an intense colour and considerable chemical oxygen demand (COD) as a result of the presence of refractory compounds which cannot be decomposed biologically and are either end products of chemical oxidation and biodegradation or are initially present in the wastewater [3-5,8].

The problem of refractory compounds elimination from industrial wastes has been intensified through introduction of closed water cycles. The following processes: coagulation, ozonization and precipitation may be used. The most efficient and least costly (cf. ozonization) are however the sorptive methods [1,2,4-6,8] with such advantages as: versatility, equipment construction and maintenance simplicity. If the volume and chemical composition of waste are constant a dynamic process with sorptive filters is used. Several methods are applied to describe sorptive filter efficiency. SONTHEIMER's indices are among

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those worth mentioning [9]: NTU (number of transfer units) and HTU (height of transfe units).

$$\mathrm{NTU} = \frac{1}{\dfrac{1}{\beta_F \cdot a_s} + \dfrac{1}{\beta_K \cdot a_s \cdot C}} \cdot \frac{\varepsilon \cdot V_k}{\dot{V}}, \tag{1}$$

$$HTU = \frac{l_F}{\mathrm{NTU}}, \tag{2}$$

$$\mathrm{HTU} = \frac{V_F}{\varepsilon}\left[\frac{1}{\beta_F \cdot a_s} + \frac{1}{\beta_K \cdot a_s \cdot C}\right], \tag{3}$$

where:

- a_s — specific surface, m^{-1},
- β_F — surface film unit transfer diffusion coefficient, m/s,
- β_K — granular unit transfer diffusion coefficient, m^2/s,
- ε — bed void ratio, 1,
- C — capacity coefficient, 1,
- V_F — filtration velocity, m/s,
- V_K — filter volume, m,
- $\dot{V}$ — load, m^3/s,
- l_F — filter lenght, m.

NTV and HTV indices give a comprehensive characteristics of sorptive filter, but they are difficult to determine in laboratory conditions. Therefore, SONTHEIMER and other proposed two factors to characterize efficiency of sorptive filters: mean unit load sorbed on filter bed until its breakthrough, as well as lenght of unused bed (LUB). The figure and the equation below explain an idea of the length of unused bed:

$$l_F = L_s + \mathrm{LUB}, \tag{4}$$

$$\frac{L_s}{l_F} = \frac{t_B}{t_{st}}, \tag{5}$$

$$\mathrm{LUB} = l_F \cdot \frac{t_{st} - t_B}{t_{st}}, \tag{6}$$

where:

- t_B — time up to the bed breakthrough,
- t_{st} — time until stoichiometric (theoretical) front reaches filter end,
- L_s — activated carbon filter length of stoichiometric load sorption.

With regard to the weight balance:

$$C_0 \cdot \dot{V} \cdot t_{st} = C_0 \cdot V_F \cdot A \cdot t_{st} = q_0 \cdot \varrho_s \cdot A \cdot l_F, \tag{7}$$

$$\mathrm{LUB} = l_F - \frac{V_F \cdot C_0}{q_0 \cdot \varrho_s} \cdot t_B, \tag{8}$$

where:

C_0 — initial concentration, mole/m^3,

q_0 — load, equivalent to C_0 concentration, mole/kg,

A — cross-section of a column, m^2,

ϱ_s — bulk density of filter bed material, kg/m^3.

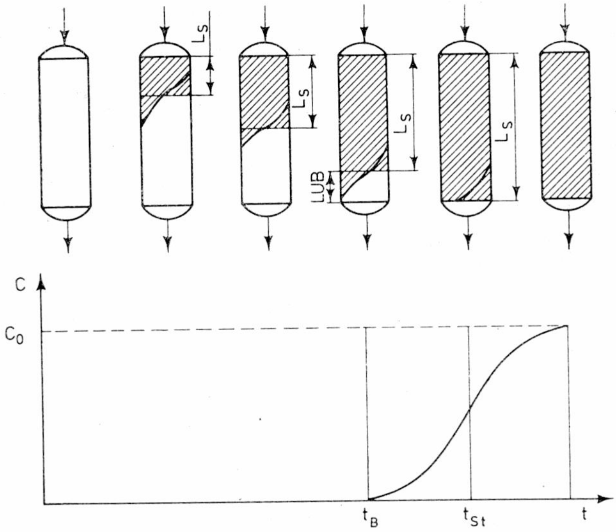

Fig. 1. Displacing of sorption front and LUB according to SONTHEIMER

Rys. 1. Przesuwanie się czoła sorpcji i niewykorzystana warstwa złoża według SONTHEIMERA

Length of unused bed depends on: sorbing agent, type of wastewater, technical conditions of filtration process and the like. LUB is present in every sorptive filter with constant bed and in most cases it reaches often several dozens percent by weight of bed length. Hence, the sorptive filter with moving bed has been considered lately as the more effective.

The present research work was carried out on two main topics: the sorptive filter — its usability in final treatment of phenol wastewater and efficiency of sorptive filters with constant and moving beds in phenol wastewater final treatment.

2. ANALYTICAL METHODS AND EQUIPMENT

Substrates used in the experiment:

Wastewater arificially prepared by dissolving phenol (C_6H_5OH) in tap water to get concentration of 300 g/m^3. It was the first part of the experiment, in which basic equations for phenol sorption were calculated.

Raw coke wastewater with chemical oxygen demand (COD) of 1680 mg O_2/m^3 and volatile phenol and steam concentration of 327 g/m^3.

Coke wastewater, chemically pretreated with calcium oxide precipitation. The amount of CaO equal to 300 g/m^3 was experimentally found to be an optimum dose. The COD of chemically pretreated wastes equaled 1590 g O_2/m^3, and phenol concentration was 286 g/m^3.

Biologically treated coke wastes with no volatile phenols present, COD equal to 378 g O_2/m^3.

Sand filter bed was used in filtration of all types of coke wastes, prior to sorption.

Granular activated carbon N used in the sorptive filters was produced by Hajnów Coal Carbonization Plant.

In order to illustrate sorptive process, the following factors were calculated: concentration of phenol and volatile phenols expressed in C_6H_5OH and COD (determined by the dichromate method) present in raw wastewater and filtrate. Phenol concentration was determined by the spectrophotometric method [10] by UNICAM 850B spectrometer, whereas COD was calculated according to ECKENFELDER [7].

Glass columns of 0.037 m inside diameter contained activated carbon filter of 0.2 m height. Columns were joined in series, thus filter bed ranged from 0.2 m to 1.6 m height. It was possible to sample filtrate for analysis from each column (fig. 2). The arrangement,

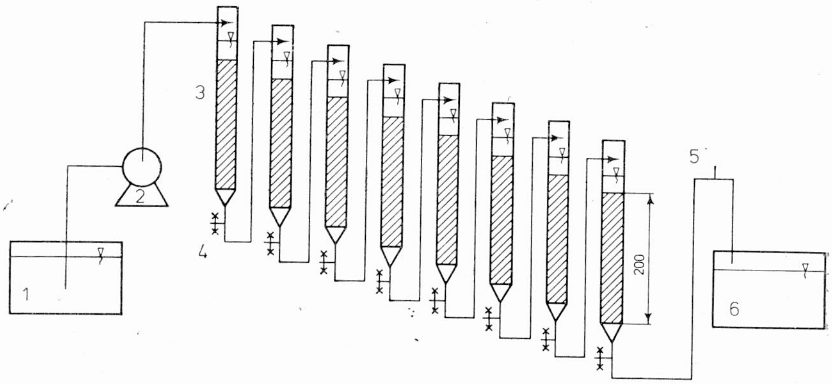

Fig. 2. Laboratory equipment pictorial diagram
Rys. 2. Schemat laboratoryjnej instalacji doświadczalnej

shown in fig. 2, was set in order to simulate sorptive process on filter with moving bed. By disconnecting the first column (from the side of wastewater inflow) and connecting the new one with an activated carbon filter (at the end of the set), the filter bed with quasi-movable (inconstant) length and definite mean flow-through velocity was obtained. When the breakthrough was observed in the filter bed of the last column, the new one was connected to the end of set, whereas the first column was disconnected when its filter bed reached a point of complete saturation, and concentration of filtrate equaled that of raw wastewater. Observations were carried out until a double replacement of the whole filter bed in sorptive filters with inconstant ("moving,,) bed, i.e. connecting 16 new columns with an activated carbon filter. The adjustment of activated carbon saturation in the first column and a breakthrough in the last column was very difficult to achieve. Therefore, it was assumed that a breakthrough of the whole filter bed took place not earlier than filter bed saturation in the first column, and the new column was connected to the set at that moment.

3. RESULTS

The observation of phenol sorption from raw wastewater on 1.6 m high filter bed was the first part of the experiment. Thus, phenol content in filtrate sampled from each column was determined and breakthrough curves for each segment were drawn. The filtration process was checked until a double replacement of the whole filter bed. Fig. 3 shows curves which were plotted for the first eight segments of the filter bed and the following five segments which were connected afterwards.

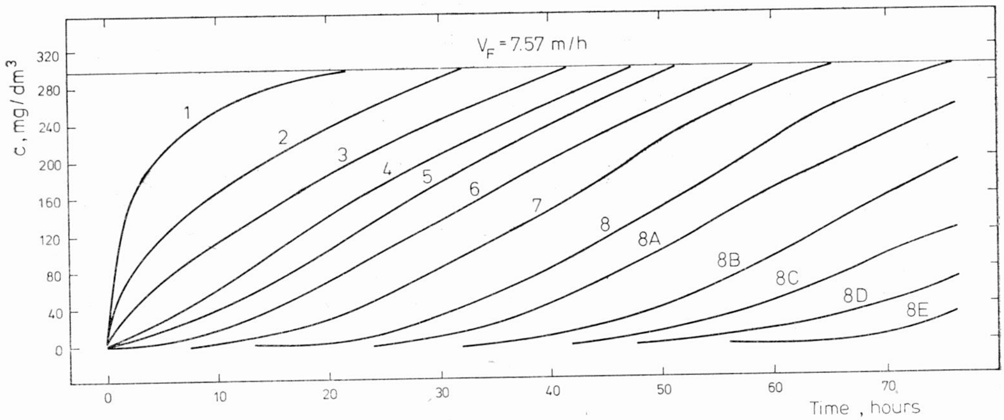

Fig. 3. Breakthrough curves of sorptive filter with mov bed segments
Rys. 3. Krzywe przebicia segmentów filtra sorpcyjnego o złożu ruchomym

Results that were obtained during the experiment helped to derive equations of variables, typical of phenol sorption on activated carbon N filter bed. The first eight segments were considered as constant filter bed of height ranging from 0.2 m to 1.6 m. Hence, mean unit load and LUB for constant filter bed were determined. Calculations were carried out for the three maximum concentrations of filtrate, such as: 10, 50 and 100 g/dm^3.

Mean unit loads sorbed on activated carbon N filter with constant and moving beds of the same height were calculated according to the following characteristics:

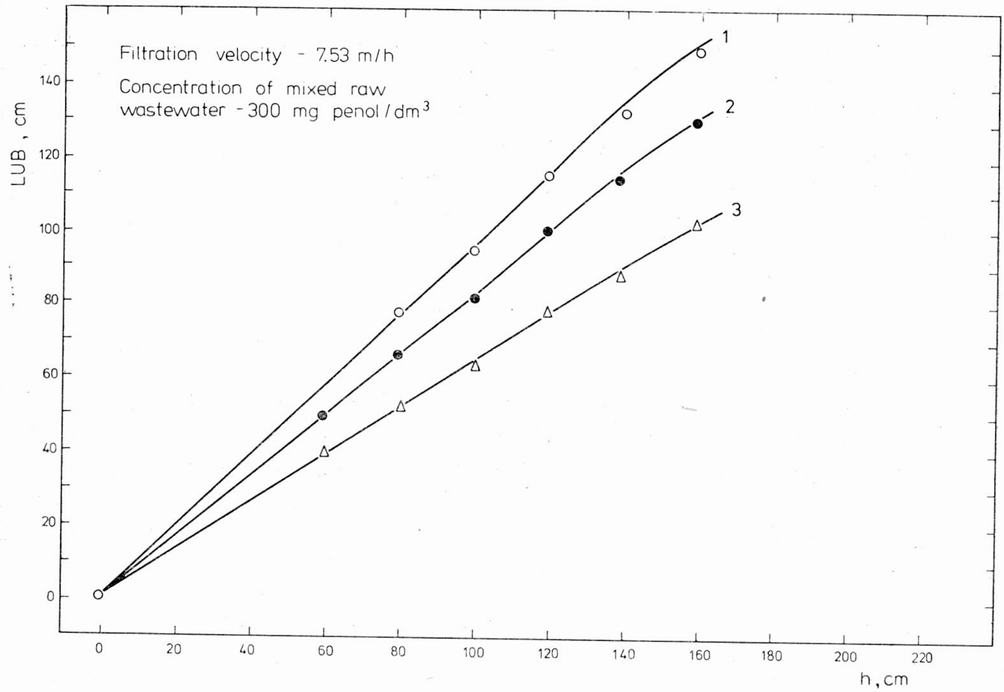

Fig. 4. Effect of sorptive bed height and maximum concentration of treated waste on LUB

Premissible concentrations of phenol in filtrate: 1 — 10 mg/dm^3, 2 — 50 mg/dm^3, 3 — 100 mg/dm^3

Rys. 4. Wpływ wysokości złoża sorpcyjnego oraz dopuszczalnego stężenia ścieków oczyszczonych na wielkość niewykorzystanej warstwy złoża

Dopuszczalne stężenie fenolu w filtracie: 1 — 10 mg/dm^3, 2 — 50 mg/dm^3, 3 — 100 mg/dm^3

breakthrough curve for filter with constant height of 1.6 m,

breakthrough curves for filter with inconstant height, when replacing 0.2 m segments with the new ones.

The results obtained from the experiment of artificially prepared phenol wastewater can be found in table.

The same examination and calculations were carried out for the following wastes:

raw coke wastewater,

biologically treated coke wastewater,

calcium pretreated coke wastewater (by precipitation).

The results compiled in table illustrate the efficiency of activated carbon N filter bed, with constant and moving beds.

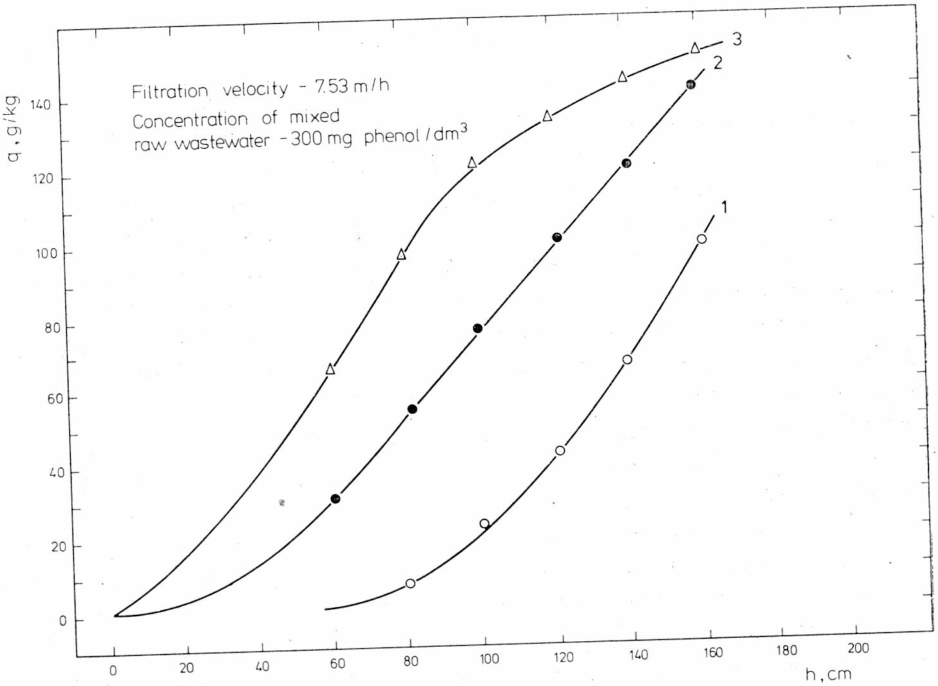

Fig. 5. Effect of sorptive bed height and maximum concentration of treated waste on the mean unit load value

For explanations see fig. 4

Rys. 5. Wpływ wysokości złoża sorpcyjnego oraz dopuszczalnego stężenia ścieków oczyszczonych na wielkość średniego ładunku jednostkowego

Objaśnienia jak na rys. 4

Table

Comparison of parameters of sorptive capacity in sorptive filters of 1.6 m height with constant and moving beds

Porównanie parametrów charakteryzujących wykorzystanie sorbenta w filtrach sorpcyjnych wysokości 160 cm o złożu stałym i ruchomym

Type of wastewater	Kind of waste-water pollution	Concentration: of raw waste-water mg/dm³	Concentration: of fil-trate (maxi-mum value) mg/dm³	LUB in filter: with constant bed, cm	LUB in filter: with constant bed, % of whole bed height	LUB in filter: with moving bed	Mean unit load: sorbed on filter with constant bed g/kg	Mean unit load: sorbed on filter with moving bed g/kg
Artificially prepared	phenol	300	10	149	93.1	0	148	276
Raw coke	COD	1680	300	97	60.6	0	478	743
Chemically pretreated coke	COD	1590	300	119	74.4	0	447	789
Biologically treated coke	COD	378	50	125	78.1	0	137	194

4. DISCUSSION

The results have confirmed that sorptive filter with constant bed is not fully utilized. Analysis of phenol sorption from artificially prepared waste points out that an increase of filter bed height brings about the rise of the mean unit load sorbed, at the same time, however, the LUB of the constant filter increases (figs. 4, 5). The two factors fully depend on the maximum concentration of pollutants in the treated wastewater. With an increase of purity degree, the load sorbed lowered, while the LUB of constant length is increased and, consequently, sorption on activated carbon is lowered. It is also, evident that there is a clear interdependance between degree of purity that is required and minimum necessary height of filter bed. Eg. for maximum phenol concentration in filtrate of 10 g/m^3, minimum height of activated carbon N filter was 0.8 m, however for phenol concentration in filtrate of more than 50 g/m^3, minimum necessary height was 0.6 m.

It seems that a suitable choice of the kind of activated carbon and the application of low filtration velocity would allow to lower LUB, although this layer will always remain in sorptive filters with constant beds. The flattening of break down curves for sucessive filter segments (fig. 3) and the increassing time required for the filtrate to achieve the permissible concentration of pollutants allow to infer that after the start up period the bed height decreases.

In sorptive filter with moving bed the LUB is practically eliminated, as the column with saturated sorbent is replaced with the new one, and the sorbed concentration is of the same value as the one of raw waste. The equilibrium is reached when the concentration of filtrate from the given segment equals that of raw wastewater. The activated carbon is then maximally utilized for the given kind of activated carbon, filtration rate, as well as for the type and concentration of pollutants in the treated wastewater.

It has been stated that when artifically prepared phenol wastewater and three kinds of coke wastes were treated in filter with constant bed height of 1.6 m, at filtration velocity of 7.53 m/h, the LUB ranged from 60.6 to 93.1% of the total sorptive bed height. The above observations speak distinctly for the sorptive filter of the movable bed, being also confirmed by the calculated unit loads (table). In each kind of wastewater examined the equilibrium load in carbon removed in quasi-continuous way from the filter with movable bed exceeded the mean load sorbed by the constant bed (the filter height being the same as in movable bed). In the first case the degree of activated carbon utilization was higher by 41% (biologically treated wastewater) and by 86% (artificially prepared phenol wastewater) than in the latter one.

It should be noted that when the wastewater contained high molecular compounds or when suspended solids were accumulated on the surface or upper layers of the sorptive bed, in a filter with constant bed mechanical clogging of carbon granules and a rapid increase of flow resistance did not allow a full exploitation of the filter. In the case of moving bed the flow resistant does not increase so rapidly, but high molecular compounds and suspension adhering partially to the subsequent segments of the filter bed decrease their sorptive capacity. This observation has been confirmed by sorption of raw coke wastes and pretreated chemically by precipitation with calcium coke wastes on the activated carbon N. Despite a slightly lowered COD, due to precipitation, the same demands required from the filtrates, the equilibrium load obtained on the filter with a moving bed exceeded that obtained on the same bed during sorption of not pretreated coke wastewater. It seems probable that precipitation with CaO removed a small part of pollutants present in high molecular forms. Hence, it follows that sorptive filters with moving beds like the filters with constant beds require that the wastewater be carefully clarified. It is admissible to remove high molecular substances from wastewater to prevent mechanical clogging of filters.

In a large sewage treatment plant where sorptive filters of moving or constant bed heights are used, an equipment for activated carbon regeneration, circulating in a counter-flow direction to wastewater, should be installed.

5. CONCLUSIONS

1. For final treatment of certain industrial wastewaters sorptive filters with activated carbon are recommended.
2. Incomplete utilization of sorptive capacity of activated carbon, occurring on sorptive filters with a constant beds, is due to the so-called length of unused bed (LUB).
3. Complete utilization of sorption capacity of activated carbon under given conditions can be achieved on sorptive filters with moving beds.
4. To ensure efficient performance of sorptive filters with moving beds, the wastewater should be carefully clarified. It is also advisable that the high molecular compounds be removed by pretreatment.
5. Application of sorptive filters with moving beds allows to close the circulation of activated carbon by installing special equipment for its regeneration.

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ZASTOSOWANIE FILTRÓW SORPCYJNYCH DO USUWANIA ZWIĄZKÓW REFRAKCYJNYCH Z NIEKTÓRYCH BIOLOGICZNIE OCZYSZCZONYCH ŚCIEKÓW PRZEMYSŁOWYCH

Przeprowadzono badania w skali laboratoryjnej, mające na celu porównanie parametrów pracy filtrów sorpcyjnych o złożu stałym i złożu ruchomym. Przy użyciu preparowanych wód fenolowych oraz ścieków koksowniczych wykazano, że w filtrach o stałym złożu, wskutek występowania niewykorzystanej warstwy złoża, sorbent nie jest w pełni wysycony. Stopień niewykorzystania sorbenta zależy m.in. od rodzaju węgla, charakteru ścieków, wysokości złoża, prędkości filtracji oraz wymaganego stopnia oczyszczania ścieków.

W filtrze sorpcyjnym o złożu ruchomym pojemność sorbenta jest wykorzystana w pełni, a ładunek zasorbowany w usuwanych z filtra segmentach złoża jest ładunkiem równowagi dla określonych parametrów prowadzenia procesu. Przemawia to za zastosowaniem filtrów o złożu ruchomym, tym bardziej, że możliwe jest zamykanie obiegu węgla na stacji oczyszczania poprzez instalację służącą do jego regeneracji.

BESEITIGUNG VON REFRAKTÄREN SUBSTANZEN AUS BIOLOGISCH VORGEREINIGTEN INDUSTRIE-ABWÄSSERN DURCH SORPTION

Im Labormaßstab untersuchte man die Sorptionsfähigkeiten eines Festbett- und eines Schwebebettfilters. Anhand von Kokereiabwässern sowie preparierten Phenolabwässern konnte man aufweisen, daß im Festbettfilter ein Teil der Schüttung nicht voll gesätigt wird. Der nicht genutzte Grad des Sorbents hängt u.a. von der Kohleart, der Abwasserart, von der Schütthöhe, der Filtrationsgeschwindigkeit sowie vom benötigten Reinigungsgrad ab.

Im Schwebebettfilter wird das Füllmaterial dagegen voll ausgenutzt, und die in den einzelnen Schüttsegmenten entzogene Menge der refraktären Substanzen ist — bei festgelegten Prozeßparametern — der Gleichgewichtsmenge gleich. Das spricht für die Anwendung von Schwebebettfiltern; in diesem Fall ist der Kohlekreislauf der Sorptionsanlage durch den Bau einer Regenerationsanlage möglich.

ПРИМЕНЕНИЕ СОРБЦИОННЫХ ФИЛЬТРОВ ДЛЯ УДАЛЕНИЯ РЕФРАКЦИОННЫХ СОЕДИНЕНИЙ ИЗ НЕКОТОРЫХ БИОЛОГИЧЕСКИХ ОЧИЩЕННЫХ ПРОМЫШЛЕННЫХ СТОЧНЫХ ВОД

Были проведены исследования в лабораторном масштабе, имеющие своей целью сравнение параметров работы сорбционных фильтров с постоянным слоем и с подвижным слоем. При использовании препарированных феноловых вод, а также коксовальных сточных вод было выявлено,

то в фильтрах с постоянным слоем, вследствие наличия неиспользованного слоя фильтра, сорбент е является полностью насыщенным. Степень неиспользования сорбента зависит, наряду с други-ди фаторами, от вида угля, характера сточных вод, высоты слоя, скорости фильтрации, а также ребуемой степени очистки сточных вод.

В сорбционнос фильтре с подвижным слоем ёмкость сорбента полность использована, а сор-ированный заряд в удаляеямых из фильтра сегментах слоя является зарядом равновесия для опре-елённых параметров проведения процесса. Это свидетельствует в пользу применения фильтров подвижным слоем, тем более, что это создаёт возможность замыкания циркуляции угля на стан-ии очистки сточных вод посредством оборудования, служащего для его регенерации.