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A METHOD OF TREATMENT OF WASTEWATERS FROM PHENOL AND ACETONE PRODUCTION BY CUMENE METHOD

A sorption method for removing phenol and its homologues from wastewaters resulting from the production process of phenol and acetone by the cumene method and for adsorbate recovery from the sorption surface has been described. At first, tar products are removed and then wastewaters are treated using sorption column filled with synthetic sorbent. Wastewater free from tar products passes through the sorption bed and reaches breakthrough point after 12 h, then column *1* is regenerated, while column *2* continues the treatment. The sorption bed is regenerated by 1.5 bed volumes of acetone and the bed is washed with recycled water. The desorbent containing adsorbate and the first volume of water is sent to the production process. The second volume of water is left for recycling. 1200 kg of adsorbate is recovered per 24 h by regeneration of the bed every 12 h.

1. INTRODUCTION

In recent years it can be noticed a widespread interest in the problem of phenolic wastewater treatment. Such factors as the large amount of phenolic materials generated as waste in water, on the one hand, and the increasing demand for pure water, decreasing water resources, loss of production materials and environmental protection standards, on the other hand, compel the investigators to connect these factors and to find a good and economic method of solving this problem [1]–[6].

For wastewaters resulting from the process of phenol and acetone production by cumene method, a technology of treatment on sorbents and the recovery of adsorbate from the sorption surfaces has been elaborated [7].

Phenolic wastewater results mainly from the neutralization of acidic mixture of phenol and acetone during the rectification of acetone in the distillation compart-

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ment. Leaks in the installation and washing the installation during repairs are the additional sources of phenolic wastewater.

A technical design of the installation of phenolic wastewater treatment was completed on the basis of laboratory and pilot plant scale investigations.

2. EXPERIMENTAL

In the laboratory tests a glass column of 45 mm in diameter and 700 mm in height was filled with 0.8 dm^3 of copolymer Amberlite XAD-4 (XAD-4) sorbent produced by Rohm and Haas Co.

In the pilot plant tests, which were performed in the petrochemical industrial plant producing phenol and acetone by cumene method, the metal columns of 150 mm in diameter and 1800 mm in height were filled with 5 dm^3 of the same XAD-4 sorbent.

2.1. SORPTION PROCESS

Clear phenolic wastewater, after removing hydrocarbons and tar products containing about 3% of phenol and 0.5% of acetone, was delivered to the top of a sorption column by means of a metering pump. The amounts of phenol and acetone in the treated wastewater after it has passed through the column were measured by ultraviolet and hydroxylamine methods, respectively. The sorption capacity being exhausted, the sorption process was stopped and the column regenerated. The next cycles of the treatment were done in the second sorption column. The rate of wastewater flow through the sorbent ranged from 1 to 6 volumes/bed volume/hour.

2.2. REGENERATION PROCESS

Regeneration of XAD-4 sorbent consists in the desorption of the adsorbate by acetone. After the removal of wastewater 1.5 bed volume of acetone was pumped to the bed from the bottom of the column. Similarly, four volumes of treated wastewater were used successively to wash the sorbent bed. Acetone eluate with adsorbate and the first volume of washing water containing about 10% of acetone were directed to the production process.

2.3. TECHNOLOGY OF THE WASTEWATER TREATMENT PROCESS

2.3.1. SORPTION OF PHENOLS

After separating the organic fraction in the tank T-1 (fig. 1), the phenolic wastewater flows into the tank T-2 where tar products and solid residue are separated. Clear wastewater is then pumped by pump P-1 to the top of the column

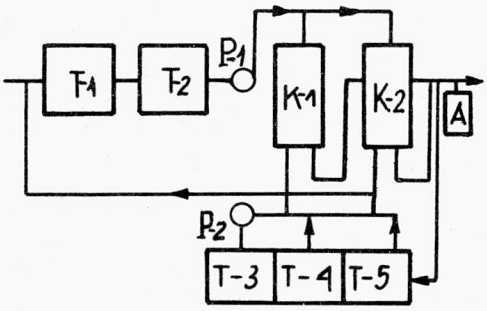

Fig. 1. Lay-out of the dephenolization process

T-1 – separator of hydrocarbon fraction, T-2 – settling tank, A – analyzer, P-1, 2 – pumps, T-3 – acetone tank, T-4, 5 – tank of water for regeneration

K-1 or K-2 filled with XAD-4. Treated wastewater is directed from the sorption column to the tank T-5, and the excess, to the biological treatment. The concentrations of phenol and acetone in the wastewater flowing out of the sorption column are continuously controlled by an analyzer. If the installation is working at full speed and untreated wastewater contains 3% of phenol and 0.5% of acetone, the sorption column becomes nearly exhausted after 12 h. Wastewater flowing out of the sorption column contains 0.04% of phenol and 0.17% of acetone (table). After the column K-1 is exhausted, the regeneration is started and sorption is continued in the column K-2.

Table

Characteristics of phenolic wastewater before and after treatment process

Parameter	Wastewater	
	Raw	Treated
Density (in the temperature of 293 K), g/m^3	1.0273	1.0252
Sulfates, %	0.350	0.330
Chlorides, %	0.004	0.004
Hydrocarbons, %.	0.252	–
Tar products, %	0.068	–
Phenol, %	2.850	0.035
Acetone, %	0.500	0.170
Solid residue, %	0.020	–
COD, mg O_2/dm^3	125021.0	14823.0

2.3.2. DESORPTION OF PHENOLS FROM SORPTION COLUMN – REGENERATION PROCESS

Wastewater left in the sorption bed is directed to tank T-1 and 0.5 volume of acetone is pumped by pump P-2 from tank T-3 to the bed. Acetone is left there for 30 min to dissolve adsorbate. One volume of acetone and water is introduced from tank T-4 to the bed and then the bed is washed with two volumes of treated wastewater from tank T-5. Desorbent and the first volume of water are directed to tank T-1, while the second volume of water after washing the bed is directed to tank T-4 and is used as the first water for washing the sorbent in the next operation of regeneration. The whole treatment and regeneration process is automatized.

3. DISCUSSION

Wastewater, resulting from the production of phenol and acetone by cumene method, contains not only phenol and its homologues but also tar products which disturb the sorption process by blocking sorbent pores. Therefore the sorption bed becomes exhausted and phenol is present in the eluate. It appears that the sorption capacity considerably decreases (fig. 2). At a 0.06% concentration of tar products in the wastewater only 20% of the sorption capacity can be utilized in the process of phenol sorption from wastewater, and the bed is exhausted after 2 h. When the content of tar products in wastewater amounts to 0.012%, and 78% of the sorption capacity is exhausted, the working time of the column in the sorption process is about 9 h. When the tar products are removed and 97% of the sorption capacity is exhausted, then – after 12 h of sorption – the bed leaks at the flow rate of 1–2 bed volume/h. At a higher flow rate of wastewater through the sorption bed the contact time of phenol with the sorbent surface is shorter and no diffusion of phenol into the inner phase of the copolymer is observed. At the flow rate equal to 6 bed volumes/h the presence of phenol in the eluate was stated after 5 h of sorption (fig. 3, curve *4*), and the pressure in the column increased due to the tightening of the bed. With regeneration media being pumped upwards, the bed is untightened and the increase of presssure is prevented.

If in the regeneration process 0.5 bed volume of acetone is for a while kept on the bed, the contact time of desorption process is extented, and the adsorbate is

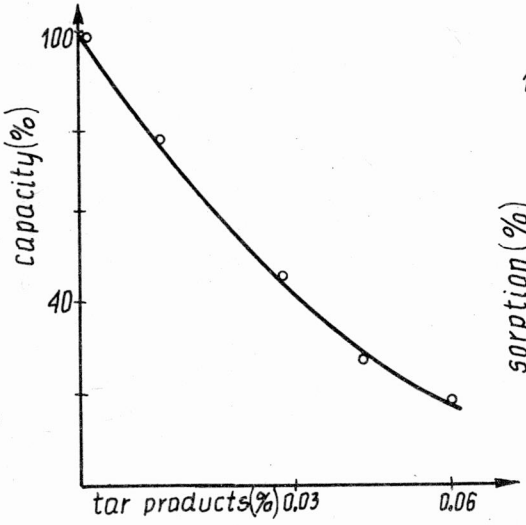

Fig. 2. An influence of tar products on the sorption capacity

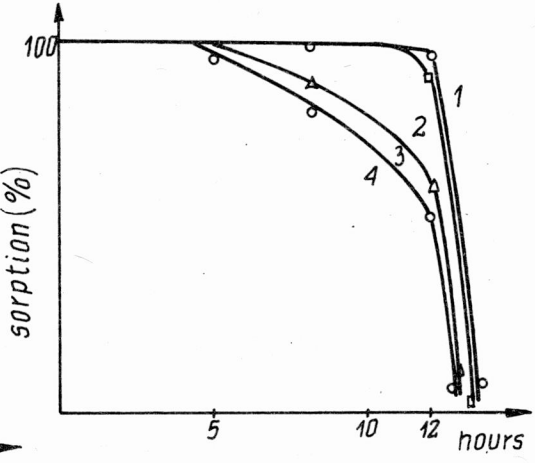

Fig. 3. Dependence of the working time of column on flow rates of wastewater

1–1 bed volume/h, 2–2 bed volume/h, 3–4 bed volume/h, 4–6 bed volume/h

dissolved. The main load of adsorbate is contained in the first half of the acetone volume (fig. 4). The contaminated eluent is washed by the next acetone volume which is removed by water. Eluate with the adsorbate and the first volume of water containig 10% of acetone and 0.01% of phenol are directed to the production process. The next water volume contains less than 0.05% of acetone and is left for washing the bed in the second regeneration cycle.

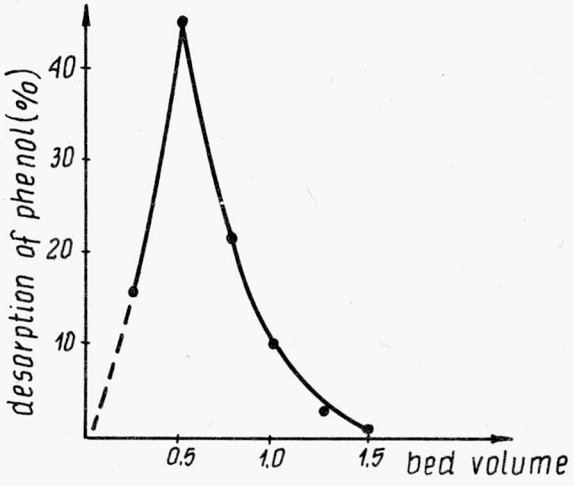

Fig. 4. Desorption of adsorbate by acetone

4. CONCLUSIONS

1. To recover 1200 kg of phenol from wastewater resulting from phenol and acetone production by cumene method two sorption column filled with 4 m^3 of copolymer Amberlite XAD-4 are used.

2. Wastewater flows gravitationally through the sorption bed at the rate of 1–2 bed volumes/h.

3. The working time of one column in sorption operation amounts to 12 h.

4. The exhausted bed is regenerated with acetone in amount of 1.5 of bed volumes and washed by 4 bed volumes of water flowing at the rate of 4 bed volumes/h.

5. Regeneration media are directed upwards into the column to untighten the sorption bed.

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OCZYSZCZANIE ŚCIEKÓW POCHODZĄCYCH Z IZOPROPYLOBENZENOWEJ PRODUKCJI FENOLU I ACETONU

Przedstawiono sorpcyjną metodę usuwania fenolu i jego pochodnych ze ścieków pochodzących z izopropylobenzenowej produkcji fenolu i acetonu. Opisano również metodę odzysku adsorbatu z powierzchni sorpcyjnej. Po usunięciu produktów smołowych ścieki są poddawane procesowi sorpcji w kolumnach wypełnionych syntetycznym sorbentem. Po 12 h pracy, kiedy jest osiągany punkt przebicia, pierwsza kolumna jest regenerowana, w drugiej zaś kolumnie jest kontynuowany proces oczyszczania. Złoże sorpcyjne jego regenerowane za pomocą acetonu w ilości 1,5 objętości złoża, następnie płukane recyrkulowaną wodą. Desorbent zawierający adsorbat oraz pierwsza objętość popłuczyn są kierowane do procesu produkcyjnego. Druga objętość popłuczyn jest recyrkulowana. W procesie regeneracji w ciągu doby odzyskuje się 1200 kg adsorbatu.

ОЧИСТКА СТОЧНЫХ ВОД, ПРОИСХОДЯЩИХ ИЗ ИЗОПРОПИЛБЕНЗОЛЬНОГО ПРОИЗВОДСТВА ФЕНОЛА И АЦЕТОНА

Представлен сорбционный метод удаления фенола и его производных из сточных вод, происходящих из изопропилбензольного производства фенола и ацетона. Описан также метод возврата адсорбата из сорбционной поверхности. После удаления смолистых продуктов сточные воды подвергаются процессу сорбции в колоннах, заполненных синтетическим сорбентом. После 12 часов работы, когда достигается порога насыщения, первую колонну регенерируют, зато во второй продолжается процесс очистки. Сорбционный слой регенерируется при помощи ацетона количеством в 1,5 объема слоя, а затем промывается рециркуляционной водой. Десорбент, содержащий адсорбат, а также первый объем смыва направляют к производственному процессу. Второй объем смыва рециркулируется. В процессе регенерации в течение суток возвращают 1200 кг адсорбата.