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DEPHENOLIZATION OF INDUSTRIAL WASTEWATERS ON THE MACROPOROUS ADSORBENT AMBERLITE XAD-4

The technology of petrochemical wastewater dephenolisation on styrene-divinylbenzene copolymer has been developed, using the methods of waste-less sorbent regeneration and sorbent and adsorbate recovery.

The principle of sorbent regeneration consists in dehumification of the bed with nitrogen and desorption of the adsorbate by using three volumes of acetone per one volume of the bed.

For 8,400 m³ of the wastewater/24 h, containing 60 mg/dm³ of phenol and 39.2 mg³ of petrochemical waste 105 m³/24 h of the adsorbent Amberlite XAD-4 are used.

The quantities of phenol and petrochemical waste recovered during 24 h amount to 504 kg and 329.3 kg, respectively.

1. INTRODUCTION

The development of chemical industry and location of new plants in the vicinity of rivers have made water purity problem still more urgent. The amount of pollutants discharged into rivers with wastewater exceeds the selfpurification capacity. A decrease in oxygen concentration and the presence of toxic substances disturb water balance.

The development of the effective methods of wastewater treatment will allow to enlarge water resources and protect efficiently water environment from pollutants.

Refinery and petrochemical wastewater treatment is especially difficult. Extractional and biological methods [4, 5, 16], [7-14], turn out to be insufficient for phenol removal. It is also indispensable to remove oil products, which at the concentration of 40 mg/dm³ form a scum on the activated sludge surface.

Laboratory tests concerning dephenolization of various types of wastewaters on ion exchangers and adsorbents proved Amberlite XAD-4 adsorbent to be the most effective for the removal of phenol and oil products.

The present paper includes:

1. Results of the investigations on the quarter technical scale technologies of petrochemical wastewater dephenolization on the macroporous adsorbent Amberlite XAD-4.

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2. The methods for wasteless sorbent regeneration, and for desorbent and adsorbent recovery.

3. Lay out of a full-scale wastewater dephenolization system.

2. EXPERIMENTAL

The testing apparatus consisted of a glass column of 60 mm in diameter and 1280 mm in height, filled with grit up to 1/3 of its height and connected in series with three sorption columns made of pyrex glass and each being filled with 0.6 dm³ of Amberlite XAD-4 sorbent produced by Rohm and Haas Co. The dimensions of sorption columns were: diameter — 45 mm, height — 1200 mm. Two adsorption columns and a gravel one were used in the phenol sorption. After two hours of sedimentation of suspended solids, wastewater was delivered to the top of the gravel column by means of a metering pump. Having passed through the column it flowed, under its own pressure, up to the top of the first adsorption column and then to the second one. The treated wastewater was directed to the receiver. Samples for the analytical control were collected from each sorption column every hour. The phenol concentration, permanganate value, COD and oil products

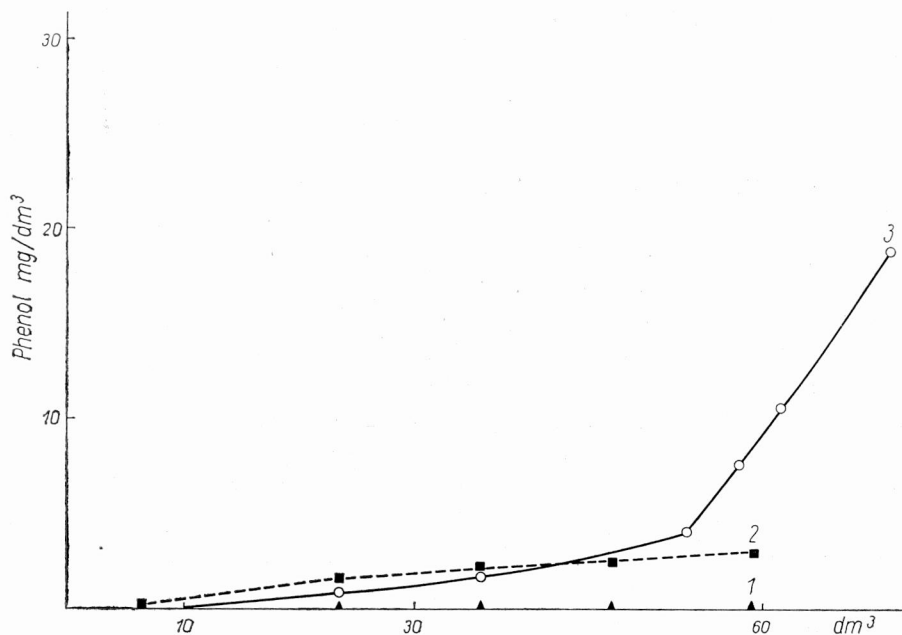


Fig. 1. Isoplans of phenol after column II

flow rates: 1 — 10 volumes/bed volume \times h⁻¹, 2 — 20 volumes/bed volume \times h⁻¹, 3 — 30 volumes/bed volume \times h⁻¹

Rys. 1. Izoplany stężenia fenolu po kolumnie II

szybkości przepływu: 1 — 10 obj./obj. złoża \times h⁻¹, 2 — 20 obj./obj. złoża \times h⁻¹, 3 — 30 obj./obj. złoża \times h⁻¹

were determined by generally accepted methods [6]. The first column was cut-off from the sorption process and regenerated when phenol concentration in the effluent reached the value of 50 mg/dm^3 (at the initial concentration of phenol in influent delivered to the first column of 60 mg/dm^3). The second cycle of wastewater dephenolization included the gravel column, as well as the second and third adsorption columns operating as the first and the second columns, respectively.

The third cycle of wastewater dephenolization included the gravel column, as well as the third adsorption column and the regenerated first adsorption column operating as the first and the second columns, respectively.

The rate of wastewater flow through the sorbent ranged from 10 to 30 volumes /bed volume/ hour. At the flow rate of 10 volumes/ bed volume /hour the concentrations of phenol and oil products did not exceed the value of 0.1 mg/dm^3 (fig. 1).

Characteristics of petrochemical wastewater before and after treatment on the adsorbent Amberlite XAD-4

	Raw	After column 1	After column 2
Density (in the temperature of 293 K)	0.9991	0.9990	0.9989
pH	6-9.5	7	8
Chlorides mg/dm^3	60	60	60
Sulphates mg/dm^3	250	250	250
Phenol mg/dm^3	60	50	0.1
Oil products /hydrocarbons/ mg/dm^3	39.2	3.8	0.1
Solid residue mg/dm^3	1050	—	—
Suspended solids mg/dm^3	90.6	—	—
COD mg/dm^3	480.8	170	60.8
Permanganate value mg/dm^3	110.0	86.0	16.2

Regeneration of Amberlite XAD-4 sorbent consists in the desorption of the adsorbent by acetone.

After the wastewater removal and drying of bed with nitrogen, three volumes of acetone were pumped to the bed from the bottom of the column. Each volume of acetone was used three times to adsorb the adsorbate from the adsorbent in the three successive elutions. The first volume of desorbent, used in the previous regeneration as the second one, was directed to the distillation. Similarly four volumes of water were used successively to wash the sorbent bed.

Acetone and adsorbate were recovered from the desorbent directed to distillation. The distillation was conducted in the 30-plate column fed at the height of $1/4$ from the

Distillation of acetone from the adsorbent X13D-4 regeneration

Fraction	g	Boiling point K	Content of the components														
			Acetone			Water			Phenol			Hydrocarbons					
			g	%	compound concentration	g	%	compound concentration	g	%	compound concentration	g	%	compound concentration			
Distillation after the first cycle																	
Acetone	1,594.0		1414.76	88.76		159.40	10.0		12.0	0.75		7.84	0.49				
Distillate	1,399.65	328.8	1397.91	99.88	88.81	1.50	0.10	0.94	0.07	0.01	0.58	0.17	0.01	2.17			
Tail fraction	194.35	368.6-369															
Water phase	166.80		9.23	5.53	0.65	152.43	91.39	95.63	5.14	3.08	42.83						
Organic phase	27.55		7.62	27.66	0.54	5.47	19.85	3.43	6.79	24.65	56.58	7.67	27.84	97.83			
Distillation after the fifteen cycles																	
Acetone	1,594.00		1414.76	88.76		159.40	10.0		12.00	0.75		7.84	0.49				
Distillate	1,399.37	328.8	1398.25	99.92	98.83	1.12	0.09	0.70	—	—	—	—	—	—			
Tail fraction	195.63	368.6-369															
Water phase	166.80		913	5.47	0.65	152.53	91.45	95.69	5.14	3.08	42.83	—	—	—			
Organic phase	28.83		7.38	26.52	0.52	5.75	20.66	3.61	6.86	24.65	57.17	7.84	28.17	100			
Distillation after the twenty ninth cycle																	
Acetone	1,599.68		1390.88	86.94		189.60	11.85		11.68	0.73		7.52	0.48				
Distillate	1,376.23	328.8	1374.35	99.85	99.87	1.73	0.13	0.91	—	—	—	—	—	—			
Tail fraction		368.6-369															
Water phase	195.35		9.04	4.65	0.65	181.31	92.78	95.63	5.00	2.57	42.81	—	—	—			
Organic phase	28.10		7.51	26.40	0.54	6.56	23.09	3.46	6.68	23.58	57.19	7.52	26.93	100.00			

top. Acetone was distilled after the first, fifteenth, and twenty ninth sorption cycles (table 1). The first two volumes of sorbent washing water of less than 10% acetone content were also distilled on the 30-plate column (table 2). Acetone, resulting from the desorbent and water distillation, was used as the third volume in the adsorbate elution from the sorbent. The data of the distillation after full-scale regeneration are presented in tables 3 and 4.

Phenol and trace amounts of oil products were

Table 2

Distillations of water +9.08% acetone

For distillation	Water	Acetone
2,000 g	1,818.4 g	181.60 g
Distillate 181.54 g	traces	181.56 g
Tail fraction 1,818.46 g	1,818.40 g	0.04 g

Table 3

Desorbent distillation after one cycle of the sorption of phenol and oil products (hydrocarbons) from petrochemical wastewater — commercial scale

Fractions	Boiling point K	Acetone		Water		Phenol		Hydrocarbons		Total kg
		kg	%	kg	%	kg	%	kg	%	
For distillation		24,944.62	86.94	3,400.14	11.85	210	0.73	137.10	0.48	28,691.86
Distillate	328.8	24,647.40	99.87	31.00	0.13	—	—	—	—	24,678.40
Tail fraction	368.6– –363									
Water phase		162.82	4.65	3,251.54	92.78	89.94	2.57	traces	—	3,504.30
Organic phase		134.40	26.40	117.60	23.09	120.06	23.58	137.10	26.93	

Table 4

Distillation of water used to wash the sorbent — commercial scale

For distillation kg	Water kg	Acetone kg
76,987.8	70,000	6,987.8
Distillate 6,986.4	traces	6,986.4
Tail fraction 70,001.4	70,000	1.4

recovered by salting out the tail fraction water phase after the eluate distillation. The organic phase, educed from the water phase, was mixed with the organic phase of the tail fraction.

3. DISCUSSION

The technology of wastewater dephenolization by sorption on the styrene-divinylbenzene copolymer Amberlite XAD-4 has been developed for the petrochemical wastewater with phenol concentration of 39.2 mg/dm^3 and flow-rate of $350 \text{ m}^3/\text{h}$. The rate of wastewater flow through the sorbent is ten volumes /bed volume/ hour.

The elution with a solvent readily miscible with water allows to recover the adsorbate from the surface of the sorbent, since phenol particles and oil products, sorbed from water solutions, are bound on the hydrophobic surface of the sorbent by Van der Waals forces.

Laboratory tests carried out previously have shown that oil products, mechanical impurities, and suspended solids, present in the wastewater affect the worktime of the sorption columns in the wastewater dephenolization process.

In the designed wastewater treatment plant (fig. 2) wastewater from the pumping station *P* is directed to the settling tank *O*. After two hours of suspension sedimentation wastewater is transported by pump *I* to the gravel column 2 and then to sorption columns (*I* and *II*) connected in series.

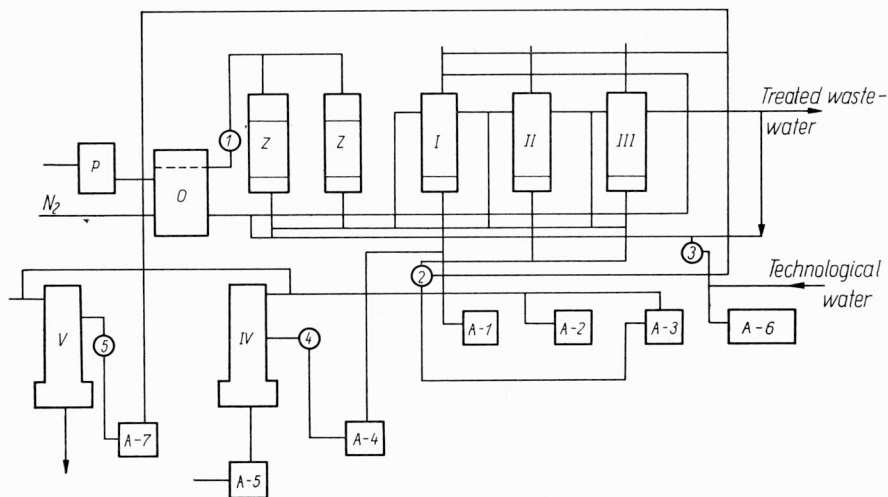


Fig. 2. Diagram of the installation for dephenolization of petrochemical wastewater through sorption on the adsorbent Amberlite XAD-4

1. *P* – pumping station, 2. *O* – settling tank, 3. *OO* – pumps, 4. *Z* – gravel columns, 5. *I, II, III* – adsorption columns, 6. *A-1, A-2, A-3* – acetone tanks, 7. *A-4* – tank of acetone with impurities, 8. *IV, V* – distillation columns, 9. *A-5* – tank of distillation residue, 10. *A-6* – tank of water for regeneration, 11. *A-7* – tank of water with acetone

Rys. 2. Schemat instalacji do odfenolowania ścieków petrochemicznych przez sorpcję na adsorbencie Amberlite XAD-4

1. *P* – pompownia, 2. *O* – osadnik, 3. *OO* – pompy, 4. *Z* – kolumny żwirowe, 5. *I, II, III* – kolumny adsorpcyjne, 6. *A-1, A-2, A-3* – zbiorniki acetonu, 7. *A-4* – zbiornik zanieczyszczonego acetonu, 8. *IV, V* – kolumny destylacyjne, 9. *A-5* – zbiornik pozostałości destylacyjnych, 10. *A-6* – zbiornik wody do regeneracji, 11. *A-7* – zbiornik wody z acetonem

The treated wastewater containing 0.1 mg/dm^3 of phenol and 0.1 mg/dm^3 of oil products is either directed to the water receivers or used as a technological water. The sorbent exhausted after the sorption of phenol and oil products is regenerated by cutting off the *I* column from the system operating in sorption. After the effluent discharge and preliminary drying of bed with nitrogen, the sorbent in the column *I* is regenerated by a desorbent supplied successively from the tanks *A-1*, *A-2* and *A-3*.

The first volume of desorbent containing desorbed adsorbate from the column *I* is taken by a pump 4 from the tank *A-4* to the distillation column *IV*. After being washed with water, the sorbent and the water are pumped, from the tank *A-7* to the distillation column *V*. The distillate from the columns *IV* and *V* is directed to the tank *A-3* whereas the tail fraction from the column *V* is used in the next regeneration process for sorbent washing.

The two-phase tail fraction after the column *V* desorbent distillation may be burnt in the fluidized-solids furnace or the organic phase-educed from the water phase by salting out may be mixed with organic phase and directed to the department producing these compounds.

Through salting the organic phase out, 36% of phenol are recovered and the water phase containing now only 6% of phenol may be discharged to the treated wastewater.

4. SUMMARY

The technology of petrochemical wastewater dephenolization by sorption on the styrene-divinylbenzene copolymer Amberlite XAD-4, as well as the methods of wasteless sorbent regeneration and desorbent and adsorbent recovery, have been developed. The testing equipment consists of two gravel columns and three sorption columns connected in series; one gravel column and two sorption columns are employed in the sorption process. When the effluent phenol concentration reaches the value of 50 mg/dm^3 , the first sorption column is cut-off and replaced with the third one. At the flow rate of 10 bed volumes per hour and for the column operation time of 10 hours the concentrations of phenol and oil products do not exceed the value of 0.1 mg/dm^3 . The treated wastewater may be used as the technological water.

Regeneration of the sorbent consists in the drying of bed with nitrogen and the desorption of the adsorbent by acetone the amount of which equals three bed volumes. Each acetone volume circulates in the three successive regeneration processes. The bed is washed with three water volumes used also in the three successive regeneration processes. The adsorbate is recovered in the tail fraction after the distillation of the desorbent. The distillation of the desorbent and water used to wash the sorbent gives acetone as a distillate. The treatment of 8400 m^3 of wastewater (with 60 mg/dm^3 of phenol and 39.2 mg/dm^3 of oil products) during 24 hours requires $105 \text{ m}^3/24 \text{ h}$ of Amberlite XAD-4 adsorbent. The amounts of phenol and oil products recovered during twenty-four hours are 504 kg and 329.3 kg respectively.

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ODFENOLOWANIE ŚCIEKÓW PRZEMYSŁOWYCH NA MAKROPOROWYM ADSORBENCIE AMBERLITE XAD-4

Opracowano technologię odfenolowania ścieków petrochemicznych przez sorpcję na kopolimerze styrenowo-dwuwinylbenzenowym Amberlite XAD-4, metodą bezściekowej regeneracji sorbentu, odzysku desorbentu i adsorbentu. Aparatura składa się z dwóch kolumn żwirowych i połączonych szeregowo trzech kolumn sorpcyjnych. W operacji sorpcji pracują: kolumna żwirowa i dwie kolumny sorpcyjne. Pierwszą kolumnę sorpcyjną odcina się i podłącza trzecią kolumnę sorpcyjną wówczas, gdy stężenie fenolu w wycieku wynosi 50 mg/dm³. Przy szybkości 10 objętości złoża/h i czasie pracy kolumny 10 h, stężenie fenolu i produktów naftowych w wycieku nie przekracza wartości 0,1 mg/dm³. Oczyszczone ścieki można używać jako wodę technologiczną.

Zasada regeneracji sorbentu polega na osuszenie złoża azotem oraz desorpcji adsorbentu za pomocą acetonu w ilości trzech objętości złoża. Każda objętość acetonu cyrkuluje trzykrotnie w kolejnych trzech operacjach regeneracji. Złoże przemywa się trzema objętościami wody używanymi, podobnie jak desorbent, w trzech kolejnych operacjach regeneracji. Adsorbent odzyskuje się w pogonie po destylacji desorbentu. Po destylacji desorbentu i wody płuczącej sorbent destylatem jest aceton.

Dla 8.4 tys. m³ ścieków na dobę o stężeniu fenolu 60 mg/dm³ i produktów naftowych 39,2 mg/dm³ ilość adsorbentu Amberlite XAD-4 wynosi 105 m³/dobę. W ciągu doby odzyskuje się 504 kg fenolu oraz 329,3 kg produktów naftowych.

DER MAKROPORÖSE AMBERLITE XAD-4 ALS ADSORBENT ZUR ENTPHENOLUNG VON INDUSTRIE-ABWÄSSERN

Besprochen wird eine neuartige Technologie zur Entphenolung von petrochemischen Abwässern mittels Sorption durch den Amberlite XAD-4 (Kopolymer des Styrols und des Divinylbenzols), die Methode der abwasserfreien Regeneration des Sorbents und die Wiedergewinnung des Desorbents und des Adsorbents.

Die Apparatur setzt sich aus zwei Kiesfiltern und drei nacheinander geschalteten Sorptionsfiltern zusammen. Die erste Sorptionskolonne wird abgeschaltet und die dritte eingesetzt, alsbald die Phenolkonzentration im Abfluß 50 mg/dm^3 überschreitet. Bei einer spezifischen Sorptionsgeschwindigkeit von 10 volumenfüllungen/h und einer Arbeitszeit einer Einheit von 10 h, erreicht die Konzentration der Phenole und Ölprodukte im Ablauf nicht mehr als $0,1 \text{ mg/dm}^3$. Das gereinigte Abwasser kann als Wasser (für technologische Zwecke) wiedereingesetzt werden.

Zwecks Regenerierung wird die Kolonnenschüttung mittels Stickstoff getrocknet; anschliessend erfolgt eine Desorption des Adsorbats mittels Azeton in einer äquivalenten Menge von 3 Volumen der Schüttung. Jede Menge des Azetons zirkuliert dreimal in 3 nacheinander geführten Regenerationen. Die Schüttung wird nachher mit drei Volumen Wasser (ähnlich wie der Desorbent) in 3 nacheinander folgenden Spülungen vom Azeton freigewaschen.

Das Adsorbat wird im Nachlauf nach der Abdestillierung des Desorbents zurückgewonnen. Das Destillat nach der Abdestillierung des Desorbents und des Waschwassers ist Azeton.

8400 m^3/d Abwasser weist eine Konzentration von 60 mg/dm^3 Phenol und $39,2 \text{ mg/dm}^3$ Ölprodukte auf. Die Menge des Sorbents Amberlite XAD-4 beträgt 105 m^3 . Täglich werden 504 kg Phenol und 329,3 kg Ölprodukte aus dem Abwasser entfernt.

ДЕФЕНОЛИЗАЦИЯ ПРОМЫШЛЕННЫ СТОЧНЫ ВОД НА МАКРОПОРИСТОМ
ДЕФЕНОЛИЗАЦИЯ ПРОМЫШЛЕННЫ СТОЧНЫ ВОД НА МАКРОПОРИСТОМ
АДСОРБЕНТЕ AMBERLITE AD-4

Разработана технология дефенолизации нефтехимических сточных вод сорбированием на стироло-дивинилбензольном сополимере Amberlite AD-4, метод бессточной регенерации поглощающего вещества, а также регенерации десорбента и адсорбата. Аппаратура состоит из двух гравийных колони и соединенных последовательно трех сорбционных колонн. При операции сорбции работают одна гравийная и две сорбционные колонны. Первую сорбционную колонну отключают и подключают третью тогда, когда концентрация фенола в элюате составляет 50 mg/dm^3 . Для скорости 10 объемов фильтра в час и продолжительности работы колонны в 10 часов концентрация фенола и нефтепродуктов в элюате не превысит значения $0,1 \text{ mg/dm}^3$. Очищенные сточные воды могут использоваться в качестве технологической воды.

Сущность регенерования сорбента заключается в осушении фильтра азотом и в десорбировании адсорбата с помощью ацетона в количестве трех объемов фильтра. Каждый объем ацетона циркулируют трехкратно — в трех очередных операциях регенерации. Фильтр промывают тремя объемами воды, употребляемыми, подобно десорбенту, в трех очередных операциях регенерации. Адсорбат регенерируют погоном после дистилляции десорбента. Дистиллят от дистилляции десорбента и воды, промывающей сорбент, является ацетоном.

Для 8,4 тыс. m^3 сточных вод в сутки, с концентрацией фенола 60 mg/dm^3 и нефтепродуктов $39,2 \text{ mg/dm}^3$ количество адсорбента Amberlite AD-4 составляет 105 m^3 в сутки. Количество фенола, регенерированного в сутки, составляет 504 кг и 329,3 кг нефтепродуктов.