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ON THE CHANGES OF SOME PHYSICOCHEMICAL PROPERTIES OF ANION EXCHANGERS USED FOR PURIFYING CHROMIUM-CONTAINING WASTEWATERS

The paper deals with the changes in some physicochemical properties of the macroporous strongly basic anion exchangers (Wofatit SZ-30, Lewatit MP-500 and Duolite A 101 D) and weakly basic anion exchangers (Wofatit AD-41, Wofatit AD-42 and Lewatit MP-62) used for purifying chromium-containing rinse wastewater of the following content: CrO_3 – 385 mg/dm^3, HNO_3 – 91 mg/dm^3, H_2SO_4 – 51 mg/dm^3.

The experimental data obtained, referring to the degree of alteration in the physicochemical properties of the ion exchangers, offer the possibility of preliminary determining the resistance of the ion exchangers, when used for purifying chromium-containing rinse wastewaters from electroplating plants.

1. INTRODUCTION

The use of ion-exchange technologies for purifying chromium-containing rinse wastewaters from electroplating plants depends to a great extent on the resistance of the ion exchangers to highly agressive compounds [1]–[3].

The degree of change in physicochemical properties of ion exchangers, used under the specific conditions of purification process, determines the possibilities of practical application of ion exchangers of various trade marks.

2. MATERIALS AND METHODS

The paper presents an investigation of the changes in some of physicochemical properties of strongly basic macroporous anion exchangers (Wofatit SZ-30, Lewatit MP-500 and Duolite A 101 D) and weakly basic anion exchangers (Wofatit AD-41,

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Wofatit AD-42 and Lewatit MP-62) used for purifying chromium-containing rinse wastewater of the following content: CrO_3 – 385 mg/dm^3, HNO_3 – 91 mg/dm^3, H_2SO_4 – 51 mg/dm^3.

The purification of wastewater is carried out under dynamic conditions (200 cm^3 volume of ion exchanger, diameter of ion-exchange columns $d=20$ mm) at a specific load of 15 dm^3/dm$^3\cdot$h. Exhausted ion exchangers are regenerated with 6 bed volumes of 5% NaOH at a specific loading of 5 dm^3/dm$^3\cdot$h.

In order to estimate the possibility of multiple usage of the investigated ion exchangers for purifying rinse wastewaters containing strong oxidizers, 20 cycles of exhaustion (with chromium-containing wastewater)–regeneration (with sodium base) were carried out.

To characterize the changes in the ionic groups and their three-dimensional polymeric skeleton, formed in contact of the anion exchangers with rinse wastewater, the following parameters of the untreated and multiply treated samples were defined: total exchange capacity (on the basis of the ion-exchange reaction: $R\text{–}OH + HCl \rightarrow RCl + H_2O$) [4], relative share of the ion-exchange groups in the strongly basic anion exchangers determined according to Martinolla's method [5] and the moisture content [6].

In order to establish the physical properties of the exchanger granules, samples of the untreated and 20-fold treated ion exchangers were subjected to 100 cycles of "osmotic shock" (one cycle includes subsequent treatment of the ion exchangers with 2 n HCl, distilled water, 2 n NaOH, distilled water) and after the 25th, 50th, 75th and 100th cycle, a microscopic scan of the ionic granules was conducted [7].

Structural porosity investigations were carried out (porosity meter "Carlo Erba", Italy) and infrared spectra were photographed (spectrophotometer "Specord M-80", Germany).

3. RESULTS AND DISCUSSION

Table 1 shows the experimental results related to the change in the value of the total exchange capacity and moisture content of the investigated samples of ion exchangers, after their repeated treatment with chromium-containing rinse wastewater.

The experimental data in table 1 shows that the exchange capacity of the treated samples of Wofatit SZ-30 and Lewatit MP-62 decreases by some 8–9% and the total exchange capacity of the other anion exchangers decreases by some 15–18%. Simultaneously with the decrease in the total exchange capacity of strongly basic anion exchangers, a certain decrease in the quality of strongly basic groups and an increase in the relative share of weakly basic groups are obvious (table 2).

It should be noted that as a result of an apparent destruction in the ion-exchange groups, after 20 cycles of exhaustion–regeneration, the capacity of the ion-exchangers against Cr^{6+} decreases by 10–15%. This influences the concentration of Cr^{6+} in the regeneration solution, and this concentration varies from 25–30 g/dm^3 after the first five cycles of exhaustion–regeneration to 22–25 g/dm^3 after the 20th cycle.

Table 1

Values of total exchange capacity and moisture content of anion exchangers before and after treatment with chromium-containing wastewater (20 cycles of exhaustion–regeneration with 5% NaOH)

Anion exchangers	Total exchange capacity (meq/cm^3)		Moisture content (%)	
	Before treatment	After treatment	Before treatment	After treatment
Wofatit SZ-30	1.00	0.92	50.0	52.4
Lewatit MP-50	1.34	1.10	51.3	52.9
Duolite A 101 D	1.20	1.00	52.0	54.3
Wofatit AD-41	1.43	1.21	54.2	56.1
Wofatit AD-42	1.24	1.02	61.3	64.6
Lewatit MP-62	2.00	1.81	53.4	55.5

Table 2

Concentration of strongly and weakly basic groups in strongly basic anion exchangers before and after treatment with chromium-containing wastewater (20 cycles of exhaustion–regeneration with 5% NaOH)

Anion exchangers	Before treatment		After treatment	
	Strongly basic groups (meq/dm^3)	Weakly basic groups (meq/dm^3)	Strongly basic groups (meq/dm^3)	Weakly basic groups (meq/dm^3)
Wofatit SZ-30	970	30	854	66
Lewatit MP-500	1295	45	1030	70
Duolite A 101 D	1175	25	956	44

These results are confirmed by the photographed infrared spectra of the untreated and treated with chromium-containing wastewaters strongly basic anion exchangers. From their analysis it is clear that the intensity of the bands of absorption of the treated samples decreases at 898 cm^{-1} and new bands of absorption appear in the area ranging from 1045 to 1180 cm^{-1}, which is a proof of the destruction of quaternary amine groups and the formation of secondary and tertiary amine groups [8].

The data in tables 1 and 2, as well as figure 1, show that the moisture content in the treated ion exchangers increases by about 2–3%, while the quantity of the

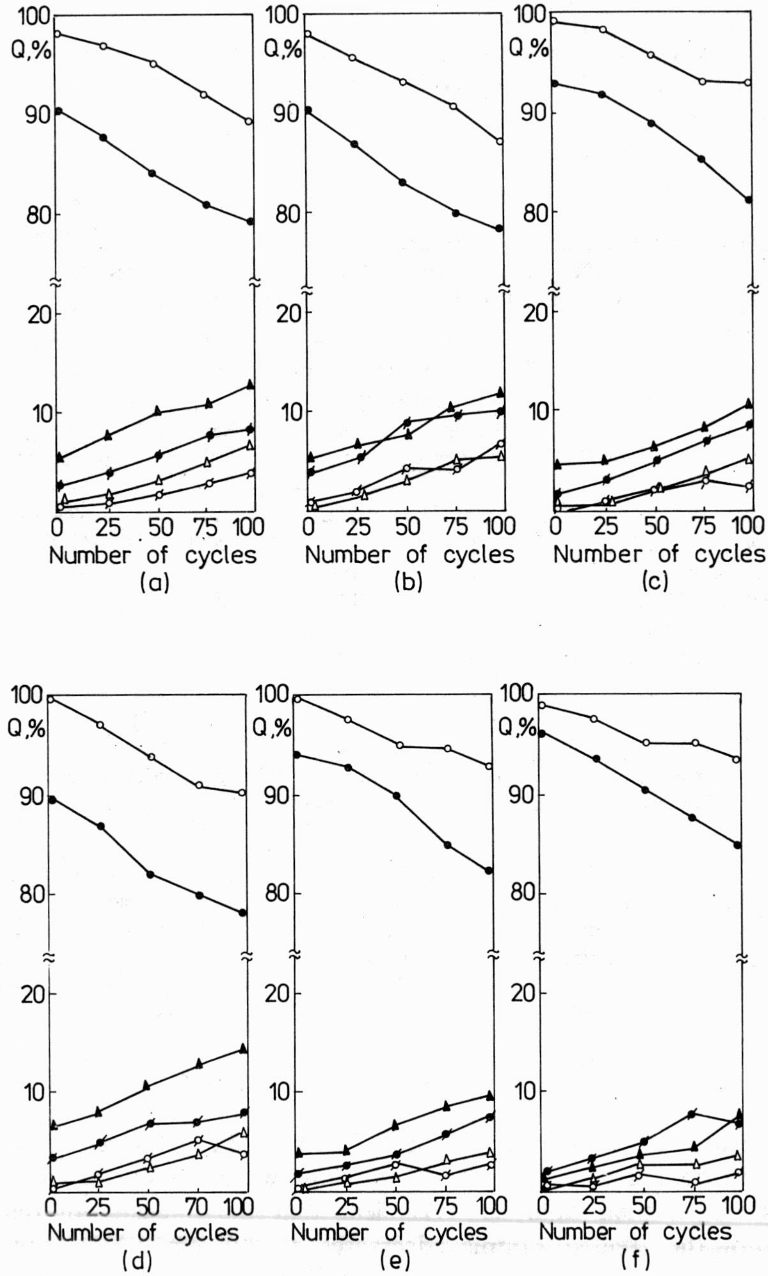

Fig. 1. Stability of ionite granules during "osmotic shock"
a – Wofatit AD-41, b – Wofatit AD-42, c – Lewatit MP-62,
d – Wofatit SZ-30, e – Lewatit MP-500, f – Duolite A 101 D
1, 2, 3 (1', 2', 3') – intact, cracked, destructed ionite granules before treatment with chromium-containing wastewater and after treatment with chromium-containing wastewater

resistant ion-exchanger granules (Q) after a hundred cycles of "osmotic shock" decreases by about 15–20%. These changes prove that the destructive alterations in the polymeric structure exist.

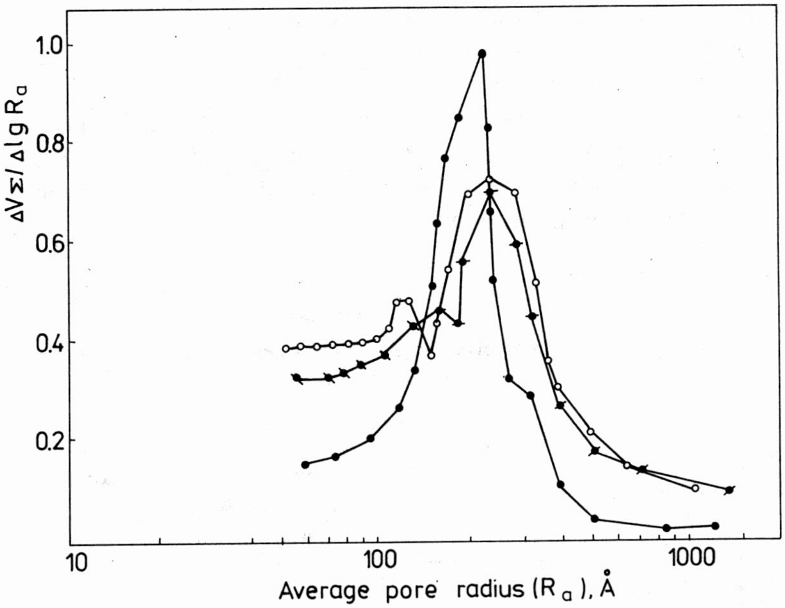

Fig. 2. Differential curve of pore size distribution in Wofatit AD-42
1, 2, 3 – untreated, treated, regenerated anion exchangers, respectively

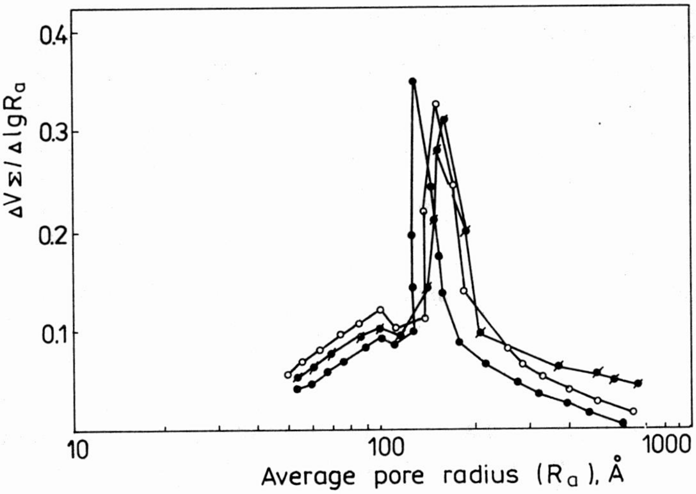

Fig. 3. Differential curve of pore size distribution in Wofatit SZ-30
1, 2, 3 – untreated, treated, regenerated anion exchangers, respectively

Comparing the infrared spectra of the untreated and treated strongly and weakly basic anion exchangers, a change in the intensity of the bands of absorption at 850–700 cm^{-1} is seen, which proves that there exist alterations in the three-dimensional polymeric structure of the ion exchangers, too [9].

Structural porosity studies allowed plotting the differential curves of pore size distribution for some of the anion exchangers (untreated, treated with chromium-containing wastewater and regenerated), (figs. 2, 3).

From the figures, it is obvious that in the case of untreated anion exchangers, pores with radii varying from 100 to 500 Å are predominant. A narrowing in the range of the radii of the predominant pores and a shift of the maximum to pores of smaller size are seen after treatment.

Table 3

Structural porosity studies of anion exchangers before and after treatment (20 cycles of exhaustion–regeneration)

Anion exchangers	Treatment	Total pore volume V_Σ (50–75000 Å) (cm^3/g)	Specific surface S (m^2/g)
Wofatit SZ-30	untreated	0.09	8.43
	treated	0.07	6.05
	regenerated	0.12	12.15
Lewatit MP-500	untreated	0.23	20.54
	treated	0.18	14.20
	regenerated	0.26	22.05
Duolite A 101 D	untreated	0.12	12.60
	treated	0.09	8.90
	regenerated	0.13	11.12
Wofatit AD-41	untreated	0.17	11.21
	treated	0.13	7.63
	regenerated	0.19	14.44
Wofatit AD-42	untreated	0.42	61.41
	treated	0.33	42.57
	regenerated	0.46	59.30
Lewatit MP-62	untreated	0.67	73.19
	treated	0.54	49.95
	regenerated	0.75	72.98

The data in table 3 shows that treatment with chromium-containing wastewater causes a decrease in the total pore volume of the ion exchangers by 20–25%; their specific surfaces are also decreased by about 30%. The above-mentioned facts prove that during purification of the wastewater, a partial filling of the pores of the ion exchangers occurs.

From table 3 it is obvious that after regeneration the pore size distribution, their total volume and specific surface area are close to those of the untreated samples of ion exchangers, which proves that the regeneration carried out leads to the restoration of the initial structural porosity characteristics of the anion exchangers investigated.

4. CONCLUSIONS

As a result of the investigations, the changes in the functional groups and the three-dimensional polymeric structures of various trade marks strongly and weakly basic anion exchangers were quantitatively characterized. The anion exchangers were subject to a multiple treatment with chromium-containing wastewater; other methods, e. g. defining total exchange capacity values, relative shares of strongly and weakly basic groups in strongly basic anion exchangers, moisture content and resistance to "osmotic shock", were also applied.

The investigations, referring to the degree of alteration of the physicochemical properties of the ion exchangers, give the possibility of preliminary determining the resistance of the ion exchangers when used for purifying chromium-containing wastewaters from electroplating industry.

The experimental data concerning the physicochemical resistances of the anion exchangers allows us to recommend the weakly basic anion exchanger of Lewatit MP-62 type for purifying chromium-containing wastewaters.

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ZMIANY PEWNYCH FIZYKOCHEMICZNYCH WŁAŚCIWOŚCI ANIONITÓW UŻYWANYCH DO OCZYSZCZANIA ŚCIEKÓW SKAŻONYCH CHROMEM

Przedstawiono zmiany pewnych fizykochemicznych właściwości makroporowatych, silnie zasadowych anionitów (Wofatit SZ-30, Lewatit MP-500 i Duolite A 101 D) i słabo zasadowych anionitów (Wofatit AD-41, Wofatit AD-42 i Lewatit MP-62) używanych do oczyszczania skażonych chromem ścieków o następującym składzie: 385 mg/dm^3 CrO_3, 91 mg/dm^3 HNO_3 i 51 mg/dm^3 H_2SO_4. Otrzymane wyniki, które dotyczą zmian fizykochemicznych właściwości wymieniaczy jonowych, umożliwiają wstępne określenie ich pojemności w przypadku oczyszczania ścieków popłuczynowych z galwanizerskich kąpieli płuczących.

ИЗМЕНЕНИЕ НЕКОТОРЫХ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ АНИОНИТОВ, УПОТРЕБЛЯЕМЫХ ДЛЯ ОЧИСТКИ СТОЧНЫХ ВОД, ИСКАЖЕННЫХ ХРОМОМ

Представлено изменение некоторых физико-химических свойств макропористых, сильноосновных анионитов (Вофатит СЗ-30, Леватит МП-500 и Дуолитэ А 101 Д) и слабоосновных анионитов (Вофатит АД-41, Вофатит АД-42 и Леватит МП-62), употребляемых для очистки искаженных хромом сточных вод следующего состава: 385 мг/дм^3 CrO_3, 91 мг/дм^3 HNO_3 и 51 мг/дм^3 H_2SO_4. Полученные результаты, касающиеся физико-химических свойств ионообменников, дают возможность предварительного определения их емкости в случае очистки промывных сточных вод из гальванических заводов.