ADSORPTION TREATMENT OF TANNERY WASTEWATER
UNDER THE ELECTRICAL DISCHARGES EFFECT

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It is known that tanning industry wastewater represents a danger to an environment because it contains a great deal of harmful organic and inorganic substances. The clearing of these waters from harmful pollutants is an important task.

The investigation results of the adsorption clearing of tanning industry wastewater from impurities with use the barrier kind electric discharge are presented in this paper.

The comparison of the wastewater chemical analysis results before clearing and after it has shown the significant decrease of the harmful impurities in the result of the electrical discharge action during an adsorption clearing process.

It was supposed that increase of the wastewater adsorption clearing intensity under effect of the electrical discharge is connected with the electrical charging of the solid adsorbent material. The experimental research of the thermostimulated relaxation (TSR) currents curves has shown that during the electrical discharge effect on the solid adsorbent the big electric charge accumulation is took place in it. The diffusion mechanism of the electric charge penetration into adsorbent material has been suggested. The theoretical analysis has shown the possibility of diffusion mechanism realization. The quantitative characteristics of electric charge diffusion process in the adsorbent material are got.

Introduction

One of the main features of tannery production is the intensive consumption of water and use the wide spectrum of chemical materials of various structures. For 1 ton of tannery processing it is required 45-50 m^3 of water that with proteins, suspended particles, trivalent and much more dangerous hexavalent chrome, sulphides, phenyl carbolic acid, chlorides, colors, fat, different organic compounds and many other materials forms the multi-component wastewater, which requires the integrated treatment [1].

To remove suspended particles there have been used methods of primary treatment allowing decreasing their content by 54-60%. Usually the chemical treatment of wastewater from above-mentioned impurities by alkali processing is more available and power-intensive. However, efficiency of purification carried out by the alkali processing is not more than 70%.

Biological treatment is the integral part of treatment plants of tannery production. The effective method of biological treatment is mixing of wastewater with biologically active deposit changing the organic compounds, nitrogen compounds and sulphides accordingly into bacterium deposit, carbonic acid gas, nitrates, nitrogen and sulphates.

Therefore, treatment of the tannery wastewater is impeded by a number of materials including it. It causes to the necessity of simultaneous use of several treatment methods [2,3].

It is known that porous adsorbents such as silica gel are use widely for adsorption treatment of the various liquids [4]. Moreover, the joint application of adsorbents and electrical discharges leads to the effective result [5].

We also suppose that use of silica gel and action by the electrical discharge will simplify considerable the technological processes and increase effectiveness of tannery wastewater treatment.

Experimental technique

In this paper the results of experimental study of the adsorption clearing of tannery production wastewater with the use of macroporous fine-grained synthetic silica gel are presented.
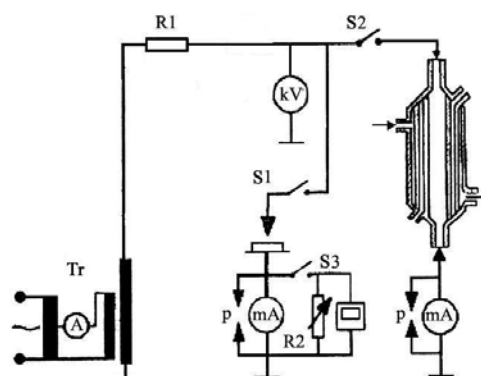

Fig. 1. Schematic electric circuit.

To increase the adsorptive capacity of adsorbents their activation by the electrical discharge of barrier type has been carried out.

Earlier it was shown that after activation of silica gel by the electrical discharge it absorbs impurities from hydrocarbon liquids more actively and proves the barrier role with respect to the number of oil products – xylene, toluene, benzol, phenolic acids and etc. [6,7].

At activation of adsorbent by the electrical discharge the filter cycle is increased and accordingly consumption of water for filter layer washing is decreased. There also decrease of full rate of filtration at repeat cycles has been shown.

At preparation stage of investigations the thermal treatment of silica gel at 200^0C with evacuation for 5 hours has been carried out. Later absorbent samples were subjected to the activation by the electrical discharge. The schematic electric circuit is presented in figure 1.

Electric discharge activation of absorbents was made in special discharge chamber, in which an electrical discharge of barrier type in interelectrode space to be excited. Treatment by barrier discharge was carried out at alternating voltage 15kV, discharge current 40mA, treatment duration 60 min.

Table 1.

Analysis results of sewage samples

| Name of indexes	Unit	Initial	Untreated	Pretreatment
PH (hydrogen ion exponent)	mg/l	12.5	10.1	8.7
Electric conductivity	mS/cm	46400	44100	32000
TDS (total dissolved solids)	Ppm(mg/l)	40600	35300	2000
$\sum_{ions}$ mineralization	mg/l	43188	43160	41516
Solid residue (105%)	mg/l	42425	40500	35950
Solid residue (150%)	mg/l	35575	32352	30000
Solid residue (600%)	mg/l	25285	22172	20780
PPP burning %	mg/l	40.4	35.6	30.4
PPP losses	mg/l	43.4	35.6	30
Cr	mg/l	4.8	2.9	0.05
Turbidity	unit/cm	3.8	2.6	0
HCO_3^-	mg/l	18.4	16	0
CO_3^{2-}	mg/l	6000	420	120
OH^-	mg/l	272	170	100
Ca^{2+}	mg/l	521	315	200
Mg^{2+}	mg/l	0	0	0
Na^+	mg/l	17377	17377	800
NH_4^+	mg/l	870	450	0.68
$NaHCO_3$	mg/l	10388	5000	150
Na_2CO_3	mg/l	10388	1875	800
NaOH	mg/l	10388	1000	120
$Ca(OH)_2$	mg/l	592.6	216	10
NH_4Cl	mg/l	2846.7	12598	1570
Sulfur compounds, oxidable by iodine (by H_2S)	mg/l	328.46	184.6	100
$\sum H_2S + HS + S^2$	mg/l	6166	5178	2694
Cl	mg/l	90000	565.7	2000
S^{2-}	mg/l	667	462	150
HS^-	mg/l	5499	5142	1500
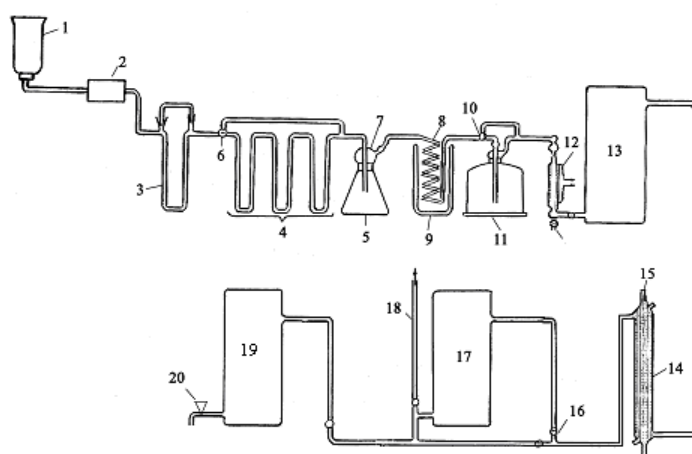
Fig. 2. Technological scheme of experiment

     1 – balloon; 2 – reducer; 3 – capillary rheometer; 4 – capillary;

     5 – 14 – elements of wastewater treatment system; 14 – reactor;

     15 – high voltage electrode; 16 –cock; 17,19 – sedimentation tanks;

     18 – atmosphere output; 20 - discharge cock.

Initial wastewater from balloon 1 through reducer 2, capillary rheometer 3 and capillaries 4 enters into the wastewater clearing system 5-14 where is cleared by the adsorption. After sedimentation in tanks 17 and 19 water through the discharge cock 20 enters in a reception container.

After the adsorption treatment processes the chemical analysis was done for the samples of treated and initial wastewater. Results of analysis are given in the table 1.

Results and their discussion

Comparing the chemical analysis results we can note that the content of impurities such as NH_4, S, HS, Cl, NaOH, Ca, NH_4Cl, $Ca(OH)_2$, Na_2S, PO_4, Na_2SO_3 and others is decreased considerably during the treatment process. For example, as it is seen from table, in initial wastewater the NH_4 content is 870 mg/l, after the adsorption clearing by silica gel without the electrical discharge treatment the NH_4 content is 450 mg/l

and after the adsorption clearing by silica gel at the electrical discharge treatment the NH_4 content decreases till 0.68 mg/l.

We supposed that increase of absorption capacity of porous absorbents under the effect of electrical discharge is caused by formation of charged state in absorbents. To reveal charged state in absorbent the method of thermo-stimulated relaxation (TSR) is used [8].

Figure 3 presents the TSR spectrum of silica gel at the linear heating of absorbent from room temperature up to 450^0C is shown [9]. From TSR spectrum it is noted that electrical discharge treatment leads to the formation of space charges of both signs in absorbents. The presence of three peaks indicates the low temperature (38^0C) and high temperature (300^0C and 438^0C) relaxation of electric charge in samples. A number of charge corresponding to the first peak is $Q=2,9x10^{-7}C$, the second peak is $Q_2=8,4x10^{-6}C$, the third peak is $Q_3=3x10^{-7}C$.
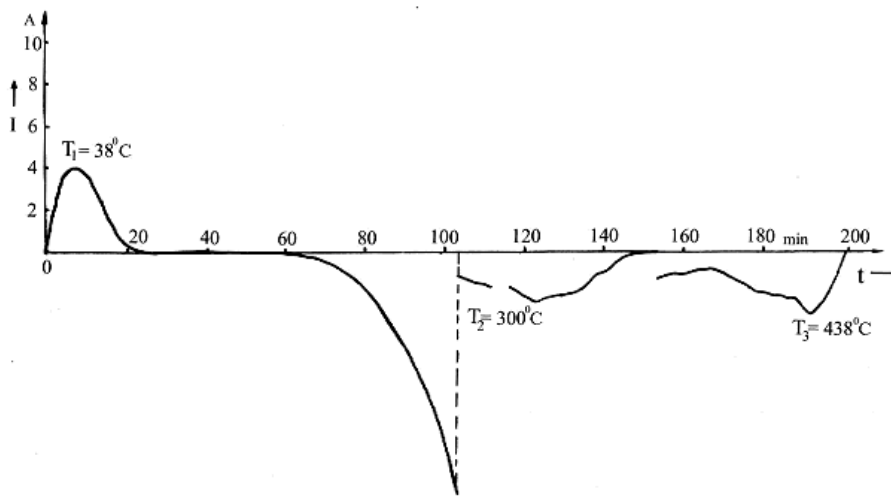

Fig. 3. Thermogram of electric charge in silica gel treated by the barrier discharge.
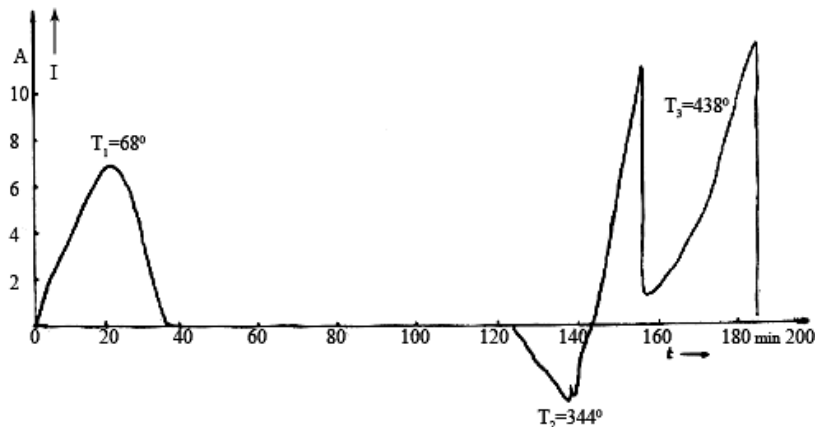

Fig.4. Thermogram of charge in silica gel in 5 months after the treatment by barrier discharge.

Our aim was to reveal whether save the electric charge on some time, introduced into adsorbent sample. For this purpose, the silica gel sample, previously treated in the identical conditions in the barrier discharge was put into hermetic ampoule, where it has been endured at the room conditions during 5 months. After it, the sample was treated by the investigations on the charge existence.

As it is seen from the spectrum comparison on fig.4, treated after the extract, the spectrum character and quantity of the relaxed charge practically hasn't changed during 5 months. This is evidence about the fact, that the charge, introduced into sample totally has saved, at least on 5 months.

It is need especially to note the following detail: repeatedly experiments on fixation of TSR spectrums, treated

in the barrier discharge (over 20 spectrums) have shown, that three peaks are revealed in all spectrums.

At that the charge quantity, corresponding to I- and III-d peaks coincides in all spectrums practically, and the charge quantity, corresponding to II-d peak is different in different spectrums.

Thus, it has been established, that activated state of adsorbents, acquired in the result of the short-time influence by the electric discharge on it, is saved during long time.

The investigations of the mechanism of the intensification influence of the electric discharge on the sorption have shown, that the adsorbent charging, established in the paper plays the significant role. The theoretical analysis of the formation of the charged state in the investigated porous dielectric adsorbents has shown that such charges state is created through diffusion mechanism of charge introduction into material structure. The values of diffusion coefficient, the value of which is between diffusion of neutral molecules, known from literature, in the investigated adsorbents and ion diffusion in non-porous identical materials, have been obtained.

This allows proposing the model of the process of adsorbent charging, according to which ions, captured by the external surface of adsorbent, diffuse into depth of the adsorbent along interstice, leading it to the charging.

The predominance of the injected charge means, that the definite mechanism of the movement of this charge into depth of silica and fixation of it inside interstice on long time exists. At the same time the significant width of TSR peaks shows, that spectrum of activation energy of the introduced carriers is also wide enough, that means in fact, that charge fixation can carry out not only inside the structure of silica substance, but on the surface of the interstice of the different sizes (micro – mezzo – macrointerstice). The mechanism of the diffusion or diffusion drift of ions is the more possible mechanism of the charge introduction inside and output of them at the thermal activation from the physical point of view.

The porous adsorbents, activated by electric discharge can be used either in pure form on direct purpose, or as the component of the compositional structures. In this and other case too for the estimation of their behavior in the electric fields it is need the value of diffusion coefficient and mobility one of ions in the structure of the porous adsorbent. In [10] on the base of the equation solution the diffusion and the comparisons of the results of the calculation with experimental data on velocity of the ion introduction into silica gel at its treatment by the corona charge has been shown, that the values of the diffusion coefficient of D_i ions in silica corresponds to the value 10^{-5}cm^2/s. In [11] the values $D_0=(1-20)\cdot10^{-5}$cm^2/s are given for the diffusion coefficient of neutral molecules. The [11] and [10] data don't contradict to each other, i.e. they are belong to neutral or ion state of the adsorbent. It is obvious, that in the case of the surface diffusion the corresponding coefficients D_i should be less, than D_0 because of the more strong connection of the ions with the surface. Thus, this fact, that $D_i<D_0$ on one-two orders can show on the prevailing role of especial surface diffusion in the process of ion transfer inside silica. As it is known, the silica presents itself the complex transformation and should be considered as the aggregate of at least three phases: the solid body with unordered structure, gas in interstice and adsorbed layer on the internal surface of

interstice. The additional meaning in favor of the surface-diffusion mechanism of ion transfer inside silica is the following: the values формула are characteristic for the total structures of that substance, from which the silica consists on $D_i=10^{-11}+10^{-13}$cm^2/s [10,12]. The values for the gas phase at normal conditions of the diffusion coefficient are equal to $10^{-1}+10^{-2}$cm^2/s [13]. If the diffusion in the particle would be simply the imposition of two processes, then at character times of the experiments, described in [10] and in present paper and consisting the decades and hundreds minutes for D_i the following values 10^{-11}-10^{-13}cm^2/s have been obtained, i.e. that characterizes the solid phase, i.e. at $D_i=10^{-2}$cm^2/s and sizes of the object not more 0,5 cm the diffusion processes in the gas are characterized by the times not more decades of the seconds. As D_i have intermediate values 10^{-6}cm^2/s , then it is naturally to consider, that we have the matter with ion diffusion in the adsorbed layer.

In the capacity of the theoretical base we use the solution of the diffusion equation:

$$\frac{d_n}{d_t} = D_i \, \Delta n \, , \qquad (1)$$

obtained in [10,13] for the spherical grain in the form:

$$n = n_0 \left\{ 1 + \frac{2a}{\pi r} \cdot \sum_{k=1}^{\infty} \frac{(-1)^k}{k} \sin \frac{k\pi r}{a} e^{-t|k} \right\}, \quad (2)$$

where n_0 is charge concentration on the surface, a is particle radius. From the value of the constant of process time

$$\tau = a^2 / D_1 \cdot k^2 \pi^2$$

In the first approximation we obtain

$$D_i = \frac{a^2}{\tau} . \qquad (3)$$

In the experiments on TSR of the introduced charges the front and the slump of the peaks forms at the simultaneous influence of the temperature activation of the charges and their diffusion drift to the marked electrodes; it is difficult to separate the influence of these factors in sum current at the temperature increase. However, if the sample can be thermostated near peak maximum, then we can consider that the further output of the charges to the electrodes has the pure diffusion character. Some quantitative error can appear in the result of the fact that the charges drift on the surface of the "transfer" interstice [11], i.e. mezzo interstice and macrointerstice, though ion adsorption itself can take place in micro interstice also. In the given article this error doesn't considered, that is equally to the fact of the prevailing role of mezzo interstices in adsorption by silica.

According to ratio (3) for D_i estimation it is enough to know the character size of the grain a and time constantτ. The experiment was carried out by the following way: the chosen particles of silica were regenerated for the creation of the equal conditions, weighted, measured as ellipsoid of revolution and further treated by discharge, the middle density in discharge current was 10mkA/cm^2 in the band of

the particle location on the electrode. The charge, taking from the discharge on the sample was estimated as 10^{-2}-10^{-3}Cl, later the electrodes were marked on the grain across short axes. Further, the grains were heated on TSR device, and the heating was switched off before the output of the maximum of the first peak and the sample was thermostated at maximum temperature. The time constant of current slump were measured on TSR current curves.

The typical curves of TSR current are presented on the fig.5. The experimental and calculative data are introduced in the table 2. Here N is sample's number, a is the half of the least size of the sample/interelectrodes space/, m and p are mass and seemed density of the sample, Q is sum charge/peak square/, T_m is maximum temperature of the first peak, $\Delta\tau$ is time of the heating till maximum, τ is time constant of current slump in minutes.
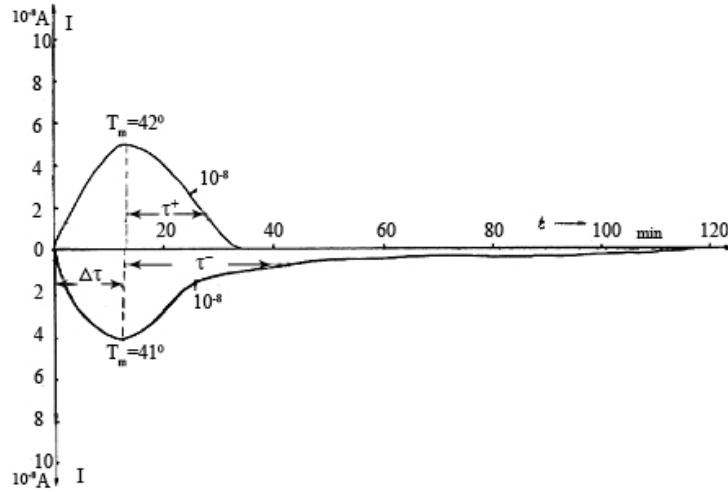

Fig.5. The curve of TSR current.

Table 2.

Experimental and calculation data

Sample No.	α cm	m g	ρ g/cm^3	Q 10^{-5} C	T_m °C	$\Delta\tau$ min	τ min	P_i cm^2/s·10^{-6}	μ_E cm^2/V·s·10^{-4}
6	0,22	0,069	0,89	+4,2	38	-	11	7,3	2,7
10	0,20	0,084	1,16	+6,9	46	17	14	4,8	1,74
4	0,24	0,089	0,88	-6,6	46	19	21	4,6	1,67
5	0,23	0,087	1,04	-8,4	43	16	21	4,2	1,54
9	0,21	0,099	1,10	-9,8	41	16	20	3,7	1,37

Though the charge value is high, but is common for TSR silica gel. The drift times depend on sign, for the positive ions $\tau^+ \approx 12$ min, for the negative ions $\tau \approx 20$ min. The diffusion coefficients and equivalent mobilities, calculated on (3) and (1) are different correspondingly. It is need to note, the obtained values D_i at the output of the charges from silica at the temperature near 40-45°C on value order coincide with values D_i obtained by [10] for the introducing ions at the room temperature. The temperature factor because of the low difference in experiment temperatures in the given case isn't significant [11]. The coincidence of the values, obtained at the introduction and the output of the charges show, that in both cases the one and the same mechanism of the diffusion drift takes place. It is need to note, that internal electric fields in silica gel are enough big. The equivalent ion mobility is equal $(1,2 \div 2,7) \cdot 10^{-4}$cm^2/V·s, at that the some difference in the mobility of the positive and negative ions is significant. As it was noted in the [10], such motilities are equal to the energies of the charge activation in hundredth and tenth parts of the electron-volt.

The calculated diffusion coefficients D_{is} in the adsorbent layer and surface mobility μ_s are needed the consideration of the real structure of silica. The values D_i and μ_E, given in the table are in fact the calculative values, which

are useable for the integral estimations, but inapplicable for the detail analysis.

As it is known, the macroporous silica gels have the sizes of the mezzointersice near 10 nm, micro porous have 2-3 nm [11]. From the ration of the initial density/density of the solid phase/silica gel (2,25g/cm^3)/ and seemed density (1,1g/cm^3) of silica gel grain is followed, that the linear sizes of the pores should be equal to the widths of the "walls" between them in almost any model image [11,14]. We can obtain for such models:

$$\frac{2dc\Lambda}{d_n + d_{ct}} = \frac{D_i}{Dis - Di}$$

where d_{ct} is width of the adsorbent layer, $d_n + d_{c\Lambda}$ is sum of the linear sizes of the pore and wall.

Designated $2dc\Lambda/(d_n + d_{c\Lambda}) = 7$, we obtain

$$D_{is} = D_i + \frac{D_i}{Z} \qquad (4)$$

If in (4) $Z \approx 0,5$, that corresponds to polymolecular adsorption in 5-10 layers and practically total filling all

mezzo interstice space by the adsorbent layer, the $D_{is}=3D_i$ and $\mu_s\approx\mu_E$. If it relatively doesn't big, for example, $\mu_s=0,3nm$ $Z\approx0,1$, that corresponds to the monomolecular or to the layer, close to it, then $D_{is}\approx10D_i$ and the values of the surface mobility μ_s are higher on the order, than equivalent mobility μ_E in the table correspondingly, i.e. $\mu_s^+\approx2\cdot10^{-3}cm^2/V\cdot s$ for the positive and $\mu_s^-<1.5\cdot10^{-3}cm^2/V\cdot s$ for the negative ions.

Conclusions

1. Thus, it has been established, that the influence of the electric discharges is intensified, processes of the liquid adsorption by solid adsorbents leads to the investigation of the selectivity of the adsorbents and their maximal adsorbent ability.

2. It has been established, that activated state of the adsorbents, obtained in the result of the short-time influence on it by the electric charge, is saved during long time.

3. The analysis of the experimental curves of TSR current of silica gel samples, treated to the working by the barrier discharge, allows measuring the values of the diffusion coefficient in silica gel, and also quantitative estimate the diffusion in adsorbent layer and ion mobility along the surface at the presence of the adsorbent layer on it.

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ELEKTRİK TƏSİRİ ŞƏRAİTİNDƏ ADSORBSİYA PROSESİ

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Məqalədə dəri emalı sənayesinin tullantı sularının yeni üsulla təmizlənməsinin nəticələri təqdim edilmişdir. Kimyəvi analizin nəticələrindən məlum olur ki, tətbiq olunan yeni üsul kifayət qədər müsbət cəhətlərə malikdir. Müəyyən edilmişdir ki, elektrik təsirləri nəticəsində adsorbentlərin həcmində kifayət qədər elektrik yükləri toplanır. Nəzəri olaraq göstərilmişdir ki, materialın elektrik yüklü vəziyyəti diffuziya mexanizmi vasitəsilə reallaşır.

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АДСОРБЦИОННЫЙ ПРОЦЕСС В УСЛОВИЯХ ЭЛЕКТРИЧЕСКИХ ВОЗДЕЙСТВИЙ

В статье представлены результаты исследования процесса адсорбционной очистки сточных вод кожевенного производства с использованием воздействий электрических разрядов барьерного вида на адсорбент. Химический анализ очищенной воды показал, что имеет место значительное уменьшение вредных примесей по сравнением с исходной водой. Методом термостимулированной релаксации выявлено образование в объеме адсорбента, обработанного электрическим разрядом, значительного количества электрического заряда. Теоретическим анализом показано, что зарядка материала адсорбента осуществляется через диффузионный механизм.