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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

MODIFICATION OF THE SURFACE OF NATURAL ADSORBENTS BY THE ACTION OF AN ELECTRIC DISCHARGE

Speciality: 3303.01 Chemical Technology and Engineering

Field of science: Technical science

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Baku – 2022

The work was performed at the Institute of Physics of the National Academy of Sciences of Azerbaijan at the laboratory "Physics and Technique of High Voltages"

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GENERAL DESCRIPTION OF WORK

Relevance and development of the work Water pollution is an essential component of all life on Earth - a global problem. Currently, the main reason for the pollution of water basins is the discharge of untreated or insufficiently treated wastewater into water bodies by industrial, textile, tanneries, soap workshops, municipal, and agriculture. The growing rates of industrial production negatively affect the ecological state of the environment, including the cleanliness of water bodies, polluting them with waste. The main existing methods of water purification are chemical methods, including the use of various chemical reagents, which themselves are environmentally harmful: water chlorination, the use of a large number of coagulants, undesirably enriching water with sulfates, chlorides, and other substances.

One of the ways to solve the problems associated with energy-saving and environmental safety is the modernization of industrial production based on new, improved technological processes, on the one hand, and the other hand, the rational use of material and energy resources. A search is underway for new, more efficient technological operations for water purification, excluding the use of reagents. Among them including the use of solid adsorbents, including those of inorganic nature, such as natural and synthetic zeolites, silica gels, and other materials that do not pollute the treated water, as well as methods that use external physical influences on the water treatment process, exposure to electric fields and discharges on processes adsorption.

Electrical methods are quite new and progressive in water purification technology. Electrical methods have significant advantages over traditional processing methods. First of all, they make it possible to abandon reagents and the necessary economy to implement this application. The ability of electric fields and discharges to have a substantial effect on various technological processes to control the properties of materials has led to their widespread use.

At present, one of the most critical problems of interest for science and practice is the study of the influence of an electric field and discharges of various origins on sorption processes. One of the promising areas of application of electric fields and discharges is the activation and modification of a surface or volume and stimulation of adsorption processes.

The effect of an electric discharge on adsorption processes is determined by the possibility of direct intervention in the adsorption process with low energy consumption, efficiency, and manufacturability. In the case of materials that are combined structures containing organic and inorganic components in the surface layer, their modification by the action of electric discharges is highly effective. Such releases include corona, barrier, flare discharges.

In connection with the large reserves of natural zeolite in the republic and scientific information about the intensifying effect of various electric discharges on technological processes, new technologies for modifying adsorbents using electric energy are urgently needed.

Research objects and subjects The subject of the study was the modification of natural adsorbents of the Aydag deposit, in Azerbaijan the large Aydag deposit is located in the Tovuz region, the reserves of which are about 28 million tons and the synthesized single-phase zeolite. The choice of research objects is based on natural zeolites' relatively cheap and affordable micro porous bodies, which are increasingly being used in practice. In addition, the choice of a single-phase synthesized zeolite is based on the fact that, in contrast to multiphase adsorbents, the adsorption processes precede differently in each phase, which complicates their analysis, single-phase adsorbents provide information on the adsorption mechanisms that characterize a specific type of adsorbent.The choice of the object of study is due to the environmental requirements of environmental protection in order to increase the adsorption processes for their use in industrial wastewater treatment processes.

Aims and purpose of the research is the modification of the surface of natural adsorbents under the influence of electric discharges, the identification of physicochemical mechanisms of sorption processes carried out under the influence of electric discharges, and, based on the results obtained, the development of a new effective adsorption process for industrial wastewater treatment.

To achieve this goal, the following tasks were set: To achieve this goal, the following main tasks were set and solved in the dissertation work:

- investigated the effect of electric discharges on the surface of natural adsorbents and synthesized single-phase adsorbent;
- the mechanism of the effect of various discharges on the surface and structure of natural and synthesized single-phase adsorbent has been studied;
- the dielectric parameters of a composite based on natural zeolite treated with an electric discharge were investigated;
- the optimal characteristics of electric discharges acting on the surface of the natural adsorbent were selected;
- Explored wastewater treatment process using the methods developed in work.

Research methods During the work, electric discharges were used, such as corona, barrier and torch discharges to modify the surface of natural and synthesized adsorbent. To determine the electric charge on the surface of the zeolite treated with an electric discharge, the method of thermally stimulated relaxation was used, which is measured and recorded as a function of temperature and time using an ENDIM two-coordinate recorder. The dependence of the change in the electrical resistivity of natural zeolite on the degree of moisture was measured with an E6-13A teraohmmeter. In order to identify the effect of electric discharge modes on the electrical and structural changes in the characteristics of the composite, an X-ray analysis was made, which was performed on an AdvanceD8 diffractometer. Measurements of the electrophysical parameters of a composite material based on natural zeolite exposed to electrical discharges were carried out using an E7-20 digital immitance meter.

Developed, proposed and designed a basic technological scheme of a plant for wastewater treatment of industrial enterprises using natural adsorbents subject to various types of electrical discharge.

The scientific novelties of the research are:

- A developed technique for modifying the surface of a natural adsorbent under the influence of electric discharges.
- They are establishing the charged state of adsorbents exposed to electrical discharges.

- X-ray results confirm the improvement of the crystal structure of adsorbents subjected to electrical influences.
- Dependence of the density of the accumulated electric charge in the adsorbent on its particle size after exposure barrier discharge.
- New electrophysical characteristics and dielectric parameters of a composite material based on a natural adsorbent - chabazite treated with an electric discharge and non-polar polyethylene PE.
- New efficient adsorptive cleaning method industrial wastewater, adsorbents exposed to electric discharge.

Scientific innovation of the research: In the dissertation work, for the first time:

- a method has been developed for modifying the surface of a natural and synthesized single-phase adsorbent when exposed to corona, barrier, and torch discharges;
- he charged state of a natural and synthesized single-phase adsorbent, formed as a result of exposure to corona, barrier and torch discharges by the method of thermally stimulated relaxation (TSR), was studied for the first time;
- it was found that under the influence of corona, barrier, torch discharges on both natural and synthesized single-phase adsorbents, their adsorption capacity significantly increases;
- structural changes, changes in electrical characteristics, an increase in the degree of crystalline and intensity of X-ray spectra, the appearance of additional pores in a composite based on natural zeolite treated with an electric discharge were revealed.

The theoretical and practical significance of the work. Based on the results obtained, a new effective process for the adsorptive purification of industrial wastewater using a natural adsorbent activated by various types of electric discharge has been developed. To obtain information about the nature and regularities of the processes of activation of the surface of a natural adsorbent under the influence of strong electric fields, a method was developed for carrying out work under conditions of exposure to electric discharges of various origins.

Approbation and application

Based on the dissertation materials, 25 scientific papers were published, including 13 articles in domestic and foreign journals, 11 in the International Scientific and Practical Conference and the 1st thesis. Scientific articles published in the following scientific journals: "Journal of Technical Physics", "Electronic Processing of Materials", "Physics and Chemistry of Materials Processing", "Energy"; "Transactions of Azerbaijan National Academy of Sciences Physics and Astronomy", "Journal of Energy Problems», «Azerbaijan Journal of Physics".

The main results of the dissertation work were discussed at the "Second International Conference on Technical and Physical Problems in Power Engineering" (ICTPE) in 2004 (Iran); at the "Third International Conference on Technical and Physical Problems in Power Engineering" in 2006 (Turkey); at the "4th International Conference on TPE" in 2008 (Romania); in 2009 at the 5th International Conference on TPE (Spain); and also reported at the scientific conference of graduate students of the National Academy of Sciences of Azerbaijan in Baku in 2009; in 2010 at the "6th International Conference on TPE" (Iran); at the "7th International Conference on TPE" in 2011 (Cyprus), at the International Scientific and Practical Conference of Young Scientists and Specialists of the National Academy of Sciences of Azerbaijan in 2014 (Baku); at the Scientific-practical conference "Modern problems of the use and management of water resources in Azerbaijan" in 2015 (Baku), at the "12th International Conference on TPE" in 2016 (Spain) and 2019 at the 15th ICTPE (Istanbul, Turkey).

The name of the organization in which the dissertation work is carried out. The presented work is part of the planned research at the Institute of Physics of the National Academy of Sciences of the Azerbaijan Republic on "Development of scientific foundations for the use of strong electric fields and discharges in technological processes."

Personal contribution of the author The scientific and practical results given in the dissertation were gained through experiments that I conducted. With co-authors, the idea for the experiments, the results acquired, and the publications published on the basis of these data were discussed.

Volume, structure and primary content of the dissertation

The dissertation consists of introduction (17951 symbols) and four chapters: I chapter (47242 symbols), Chapter II (27742 symbols), Chapter III (58260 symbols), Chapter IV (21437 symbols), main results (2370 symbols), a list of used scientific literature in 117 titles and has a volume of 155 pages. The thesis includes 40 figures and 11 tables. The total number of characters is 178608.

MAIN CONTENT OF WORK:

The introduction shows the relevance of the topic of the dissertation, formulates the goals and objectives of the research, and notes the scientific and practical significance of the work.

2. Modification of surface sensors under the influence of electric discharges. The first chapter provides an overview of works devoted to the current state of adsorption processes at the liquid-solid interface and an analysis of the technical literature on the effect of various types of electrical discharges on solid surfaces, sorption processes.

The review describes the processes occurring on the surface of sorbents, the mechanism of adsorption, and the surface structure of various adsorbents. In the process of adsorption, there are forces similar to the nature of the forces involved in chemical interaction. On the surface of adsorbents, there are areas with free residual valences. If the adsorbed molecule hits the corresponding unoccupied active center of the surface, the molecule binds to the latter. Under the discharge action, the molecules of substances are ionized, and the process of binding with the surface of the adsorbent is facilitated.

More than 30 natural zeolites and their deposits are known, which are convenient for industrial processing. The most common natural zeolites: chabazite, mordenite, clinoptilolite.

The literature analysis showed that modification of the surface and structure of porous materials increases the selectivity of adsorbents and is one of the directions for regulating their structural and physic mechanical characteristics.

The electric-discharge modification of some dielectric and composite materials was studied. There is a change in their bulk properties, namely, the appearance of a charge state in inorganic porous adsorbents and their polymer compositions. Studied the formation of a charged state in inorganic porous adsorbents - silica gel, clinoptilolite zeolite, and a polymer composition - a natural adsorbent and non-polar polyethylene

Also, various types of technological impact on materials are considered in detail, of which electrical technology is of particular interest. Finally, based on the analysis of literature data, the problem statement is formulated.

2. Technique for conducting studies of the activation of the surface of a natural adsorbent under the influence of electric discharges. The second chapter describes the experimental setup and the rationale for choosing a subject and research methods. The developed methods of surface modification of natural and single-phase synthesized adsorbents under the influence of various electric discharges are described. The issues of the choice of adsorbents, the type and modes of electrical action on the adsorbent are considered. A current-voltage curve is presented, a developed method for analyzing the charge state of adsorbents, X-ray diffraction pattern, thermally stimulated relaxation (TSR). Laboratory installations with specially designed absorbers and electrical circuits are presented, allowing various types of discharge. The fundamental technological schemes of a facility for wastewater treatment of various industrial industries are describe

The experiments were carried out without the imposition of an electric discharge and in the field of various shots at the selected voltage range. Several release types were used to activate the selected objects: barrier, corona, and torch.

A barrier discharge is initiated in a narrow cavity between two electrodes. To limit the current density and uniform distribution of the discharge along the electrodes, a dielectric is introduced into the working zone of the release, which, with a sufficient thickness, can become the processed material itself. Barrier discharge possesses superior technology, as it allows the process of relatively large surfaces of materials that pass through the discharge interval.

A reactor was used to obtain an electric barrier discharge, which structurally is a system of two coaxial glass cylinders inserted into one another. The adsorbents under study were placed in the space between the two cylinders. The length of the reactor is 130 mm; the length of the discharge gap is 4 mm. The active zone during the barrier discharge is concentrated directly at the surface of the adsorbent. The adsorbent was activated at an alternating voltage $U = 15$ kV, discharge current $I = 70$ μA, activation time $\tau = 1$ hour.

Like a barrier discharge, an electric corona discharge inside an adsorber with a sharply inhomogeneous field configuration arises at a voltage across the electrodes $U = 11$ kV. Corona discharge is a high-voltage self-discharge that occurs in a highly non-uniform electric field at relatively high gas pressures. The main feature of this discharge is that ionization processes do not occur along the entire length of the gap but only in a small part of it near the electrode with a small radius of curvature. This zone is characterized by significantly higher field strength values than the average values for the entire gap; a corona discharge occurs in the electrode between the plane and the tip. The voltage is higher on the needle than on the plane and thus less effective than the barrier discharge. The adsorbent activation conditions were as follows: voltage $U = 13$ kV, discharge current $I = 40$μA, activation time $\tau = 1$ hour. Before electrification of the sorbent samples, the areas were ground on two opposite sides of the sorbent. The method of thermal vacuum deposition the aluminum electrodes of a round shape with a diameter of 3 mm and a thickness of (3-4)μ.

The torch discharge is a single-electrode high-frequency discharge, and the ionization zone covers the entire interelectrode gap. In contrast to a corona discharge, the ionization zone covers the whole interelectrode gap in a torch discharge. Unlike a barrier discharge, it can fill large gas volumes using special multi-touch processing devices. This makes the torch discharge particularly promising for processing materials in dispersed form (powders). Conditions for activating the adsorbent under the influence of a torch discharge: the value of the applied voltage at a constant voltage U = 15 kV; discharge current I = 70 μA; time of exposure of the release to the adsorbent τ = 1 hour, the distance between the upper electrode to the surface of the tablets d = 5 cm.

To reveal the charged state in the adsorbent, the method of thermally stimulated relaxation (TSR) was used, the charged state was recorded on an ENDIM device.

3. Study of the effect of an electric discharge on the electrophysical properties of a natural adsorbent. The third chapter presents the results of a study of the effect of various electrical discharges on the surface condition and the electrophysical properties of natural and synthesized adsorbents. The results of studies on the formation of a charged state in natural zeolites under the influence of an electric barrier, corona, and torch discharges are shown.

It was found that during the electric-discharge treatment of the samples; additional centers are formed, which leads to an increase in the volume of the sorbing pores of the sorbents, thereby contributing to a significant increase in their adsorption capacity.

It is known that, under the influence of strong electric fields and discharges, an electric charge is formed in adsorbent samples. Furthermore, studies of the mechanism intensifying the effect of an electric discharge on sorption have shown that the amount of the adsorbent plays a significant role in this process.

A theoretical analysis of the formation of a charged state in the investigated porous dielectric adsorbents showed that such a charged state is formed through the diffusion mechanism of the introduction of charges into the material's structure. Furthermore, the diffusion coefficient values were obtained, the value of which is in the interval between the diffusion values of neutral materials in the studied adsorbents and the diffusion of ions in non-porous identical materials. This made it possible to propose a model of the adsorbent charging process, according to which ions captured by the outer surface of the adsorbent diffuse into the depth of the adsorbent along with its pores, leading to its charging.

To identify the reasons for the increase in the adsorption capacity of natural zeolite, the formation of a charged state in them was studied, and an X-ray analysis of the initial and activated adsorbents was carried out. An analysis of X-ray diffraction patterns shows that the untreated adsorbent has a semi-crystalline structure, the crystal framework of which contains essentially amorphous impurities, and in the treated samples, with an increase in the time of electric-discharge processing, the degree of purification of the crystal framework from impurities increases due to the process of emission from the surface, which leads to an increase in the intensity of X-ray scattering. And also, the analysis of X-ray spectra shows that new phases are not formed after processing the adsorbent. Specifically, it has been shown that the electrical processing of materials triggers the processes of destruction and or cross linking. In addition, the polarization in an electric field occurs, i.e., electrical charges penetrate the subsurface layer or the volume. In other words, the material is modified. In the material being processed, new voids appear (apart from some other effects); the amount of pores increases. The increase in the number of pores is confirmed by the decrease in the values of the dielectric parameters, such as the capacitance, permittivity ε, dielectric losses *D*, etc. The crystallinityof the adsorbent grows because of the increase in both the percentage of the crystallinephase (with sacrifice in the amorphous phase) and the formation of new crystalline structures.

A feature of the barrier discharge is the local accumulation of charge on the surface of the dielectric barrier during the development of each spark, which was revealed by the TSR method on adsorbents (Fig. 2 a, b, c).

The spectra of thermally stimulated relaxation in a barrier discharge of ac voltage were recorded for clinoptilolite (Fig. 2.a), natural chabazite (Fig. 2.b), and a single-phase adsorbent (Fig. 2.c). Value of the electric charges:

Clinoptilolite:
T_1=350ºCQ_1=$2,9\cdot10^{-5}$ C; T_2=400 ºCQ_2=$3\cdot10^{-5}$ C;
T_3=420 ºC Q_3=$1,3\cdot10^{-5}$C; T_4=510 ºC Q_4=$2,7\cdot10^{-5}$ C.
Natural chabazite:
T_1=320ºCQ_1=$1,1\cdot10^{-6}$ C; T_2=370ºCQ_2=$4,1\cdot10^{-7}$ C;
T_3=500 ºCQ_3=$5,6\cdot10^{-6}$ C.
Single phase chabazite:
T_1=300°CQ_1=$7,5\cdot10^{-7}$C;T_2=320°C Q_2=$7,5\cdot10^{-7}$C,
T_3=370°CQ_3=$2,6\cdot10^{-7}$ C; T_4=510°C Q_4=$2,5\cdot10^{-6}$ C.

It was revealed by the TSR method that under the action of an electric barrier discharge on natural and single-phase zeolites, the formation of a charged state, free movement of charged particles on the adsorbent surface, and local charge accumulation on the surface of adsorbent samples are observed.

To determine the formation of localized charges under the action of an electric discharge on the adsorbent, we carried out studies of powdered clinoptilolite with various particle sizes in the field of a barrier discharge. The data obtained on the charge states in samples with different particle sizes are presented in Table 1.

Table 1.
The accumulated charge values in samples with different particle size

№	d, mm	T_1, °C	T_2, °C	T_3, °C	T_4, °C	Q_1, C/cm^2	Q_2, C/cm^2	Q_3, C/cm^2	Q_4, C/cm^2
1	0,4	280	380	420	500	$5,3\cdot10^{-8}$	$5,3\cdot10^{-8}$	$2,6\cdot10^{-8}$	$2\cdot10^{-9}$
2	0,25	320	420	510		$5,7\cdot10^{-7}$	$1,6\cdot10^{-7}$	$1,6\cdot10^{-7}$	
3	0,063	290	420	480		$6,9\cdot10^{-6}$	$9,4\cdot10^{-6}$	$5,2\cdot10^{-6}$	

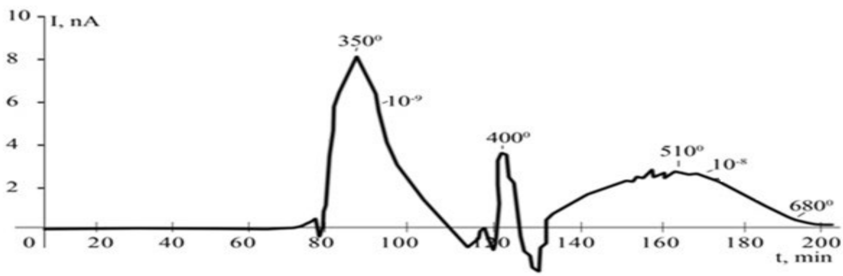

Fig.2 (a).Their curve stimulated current versus time for clinoptilolite treated with a barrier discharge.

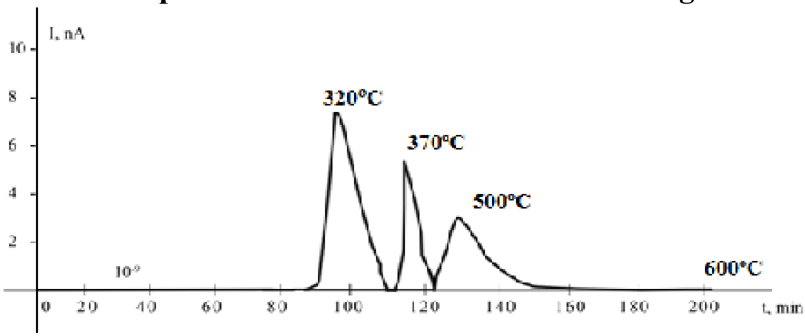

Fig.2 (b).The curve of the dependence of the thermally stimulated current on time for natural chabazite treated with a barrier discharge.

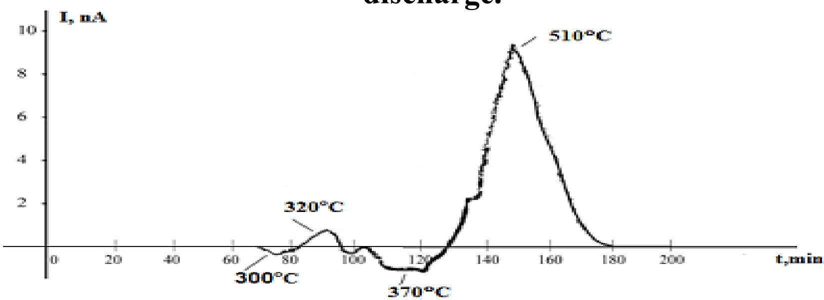

Fig.2 (c).The curve of the dependence of thermally stimulated current on time for single-phase chabazite treated with a barrier discharge.

From table 1, it can be seen that with a decrease in the particle size of the samples, the amount of charge accumulated in them by the action of an electric discharge increases. This fact is explained by the fact that with a decrease in the size of the adsorbent particles, the surface treated by the electric discharge increases, which leads to an increase in the charge accumulated in the material[1]

X-ray and physical analysis found that the processes of polarization, the introduction of electric charges directly onto the surface or into the bulk of the material, lead to the appearance of bound electric charges; that is, a charged state is formed in the material.Experimental studies were carried out to study the dielectric parameters of a composite synthesized on the basis of a natural adsorbent and unprocessed non-polar polyethylene treated in an electric field of a barrier discharge. The composites were prepared from a homogeneous mixture of powders by hot pressing. The percentage contents of chabazite and polyethylene were 20% and 80%, respectively. In addition, characteristics I–V were found for all samples at room temperature (T = 300 K). (Fig.3, 4).

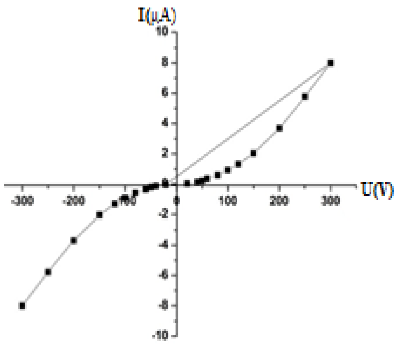

Fig.3.I-V characteristic of an untreated sample ($U=200V$ $I_1=3\mu A$).

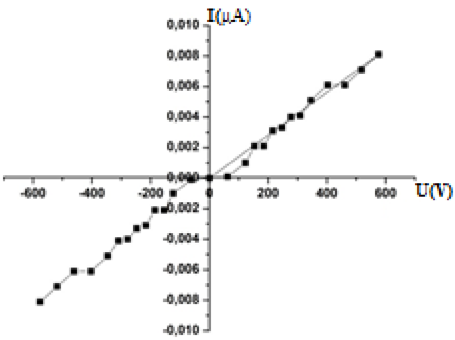

Fig. 4. I -V characteristic of the processed sample ($U=200V I_1= 0,002\mu A$).

[1]Гашимов, А.М. Размерный эффект при образовании зарядового состояния в частицах природного клиноптилолита под воздействием электрического разряда / А.М.Гашимов, К.В. Гурбанов, Р.Н. Мехтизаде, И.Г. Закиева,М.А.

As can be seen from the figures, the dependence of the current value I = f (U) on the applied voltage value is a nonlinear-character.The electric current is very different with the same value of the applied voltage U = 200V.

It was found that the wind in the unprocessed samples is 1500 time higher than in the sampled discharge-processed for one h. The current in the former models is high because of defects and foreign impurities present in the natural adsorbent. A decrease in the value of the electric current in composites with treated adsorbents indicates that the treatment in an electric discharge modifies the electrophysical properties of the adsorbent [2].

To further clarify the effect of electrical treatment on the adsorbent's electrophysical properties, the electric current's dependence on the time of exposure to the applied voltage (degradation-aging of the composite) was investigated. The degradation of composites was studied at a constant voltage U=100V for 6 hours at room temperature.

The experimental results are shown in Fig. 5 (a, b), from which the following conclusions can be drawn: In Figure 5 (a), the current in untreated samples decreases strongly with increasing time and is exponential.

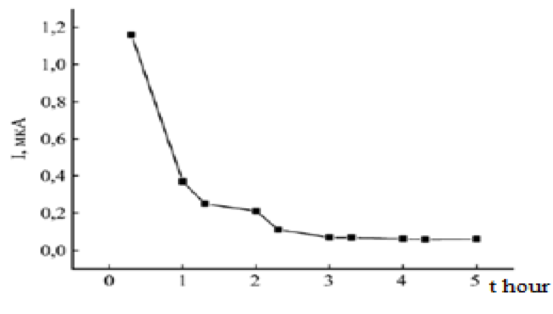

Fig.5 (a). Time dependence of the current of injected charges: a) untreated adsorbent

[2] Гашимов, А.М. Влияние электрических обработок на электрофизические характеристики природного адсорбента / А.М.Гашимов, И.Г. Закиева //Электронная обработка материалов,- Кишинев:- 2016.Т. 52, №5, с. 58-62.

In fig. 5 (b) the magnitude of the current in composites based on those treated with an electric discharge, within two hours, increases strongly with increasing time, reaches a maximum value, and then decreases with increasing exposure time.

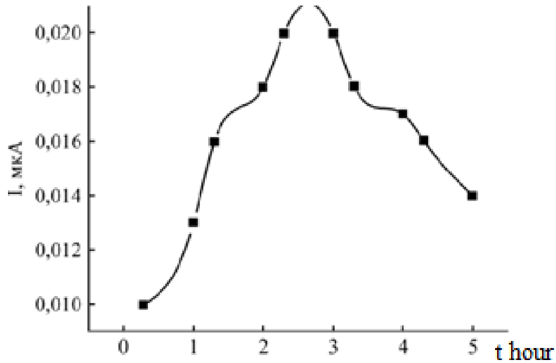

Fig.5 (b). Time dependence of the current of injected charges: b) an adsorbent treated with an electric discharge (τ_1= 1 hour)

A decrease in the current in the test sample with time indicates that the electrical conductivity is due to charges (including ions) of foreign impurities, which are reduced due to the electrical cleaning of the material. As the charges move deep into the composite, current carriers are captured by unevenly spaced shallow traps created by various impurities and structural defects; as a result, the concentration of current carriers and, as a consequence, the electrical conductivity of the composite decreases.

As can be seen from the formula (1), the electrical conductivity is determined by the concentration and mobility of current carriers. Considering that the value of mobility in composites is low, and then an increase in the concentration of current carriers should play the main role in the increase in conductivity.

$$\sigma = en\mu \quad (1)$$

Where: e - is the electron charge, n - is the charge carrier concentration, and μ - is the carrier mobility.

As shown in Fig. 5 (a), as shallow traps are filled, the dependence I= f (τ) monotonically decreases with increasing time and stabilizes. An increase in the current value with time in Fig. 5 (b) indicates the participation of charges in the composite, which are the structural elements of the material itself. A decrease in the current after the maximum I = f(τ) is associated with the capture of charge carriers by deep traps.

First, it should be noted that when the transport properties of inhomogeneous materials are analyzed, much attention is paid to the dispersion of dielectric parameters (permittivity, dielectric losses, etc.). Despite the variety of inhomogeneous matrix media used in various fields of science and technology, they all are polarized by the Maxwell - Wagner mechanism. This polarization is macroscopic (or surface, interlayer, charge volume, interfacial, etc.) due to the charged surface layers that arise at the interface between different media when free charges move within the composite phases under the action of an applied electric field. The frequency dependence of the dielectric parameters, i.e., the real and imaginary parts of the complex permittivity, is the material characteristic and is determined not only by the properties of molecules of the material but also by the presence and composition of impurities.

The results of calculating the dependences of dielectric losses on the frequency and electrical conductivity values on frequency are shown in Figures 6 and 7.

The frequency dependence of dielectric parameters is a characteristic of the material. Comparing the figures revealed the following features of the investigated composite based on natural adsorbent and polyethylene. Dielectric losses D in the unprocessed sample are almost three times greater than in the processed one at low frequencies. In the unprocessed sample, D first strongly decreases with increasing frequency (Fig. 6), reaches a minimum, then grows to a maximum at f = 104 Hz.[3]

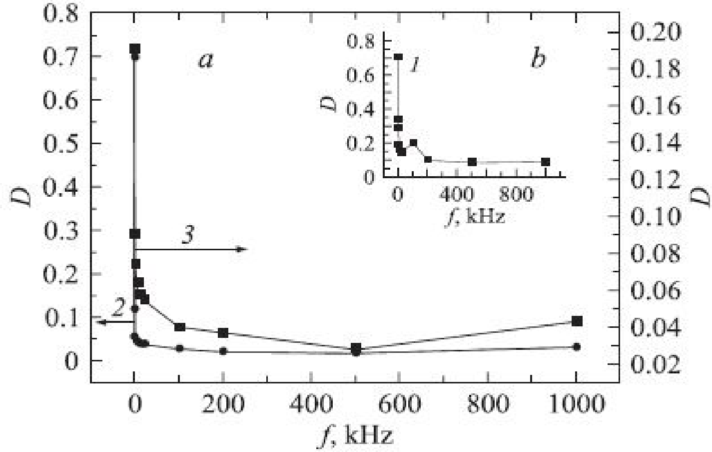

Fig. 6.Dielectric losses vs. frequency: (*1*) unprocessed adsorbent, (*2*) adsorbent discharge-processed for one h, and (*3*) adsorbent discharge-processed for two h.

Can explain the decline of the permittivity and dielectric losses with increasing frequency and. As the frequency rises, the first one and then other charged particles (relaxation oscillators) fail to reach localization sites within the quarter-period of the applied variable electric field and, permanently following the electric field variation, contribute to the conductivity (Fig. 7).

Comparing curves *a* and *b* in Fig. 7, one can see that conductivity σ of the unprocessed sample (curve *b*) is almost ten times higher than σ of the sample processed for one h (curve *a*). At low frequencies, the conductivity first monotonically grows and then sharply increases with frequency by the law σ ~ f 0.8.The relationship σ ~

[3]Gashimov, A.M.Dielectric parameters of composites based on electric discharge processed natural zeolite / A.M. Gashimov, I.G. Zakiyeva // Technical Physics, ISSN 1063-7842, - 2017, -Vol. 62, -No. 9, - pp. 1381-1384

f 0.8 indicates that conduction is due to the charge transfer between states localized in the neighborhood of the Fermi level[4]

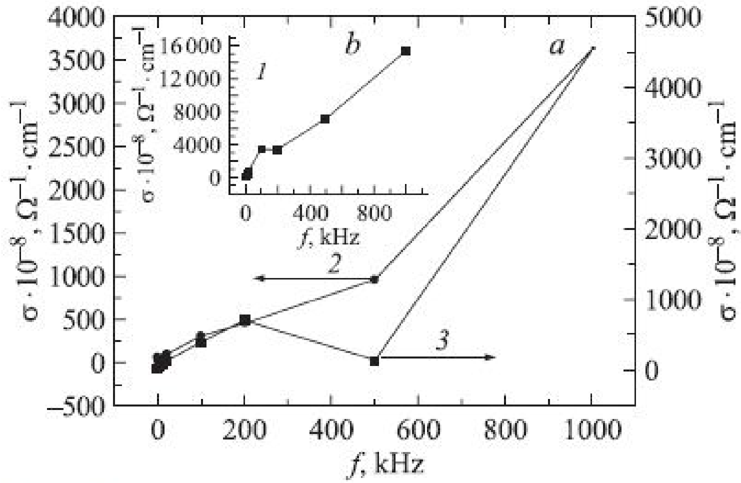

Fig. 7.Conductivity vs. frequency: (*1*) unprocessed adsorbent, (*2*) adsorbent discharge-processed for one h, and (*3*) adsorbent discharge-processed for two h.

The difference between the conductivities is so great that the electrical treatment that purifies the adsorbent reduces the number of charge carriers and thereby reduces the conductivity σ together with the real part ε' of the permittivity. This agrees with the experimental data (Fig. 8):

The results of studies and experiments have shown that the effect of an electric barrier discharge on a natural zeolite leads not only to its structural changes, but also to changes in its electrical characteristics and dielectric parameters.

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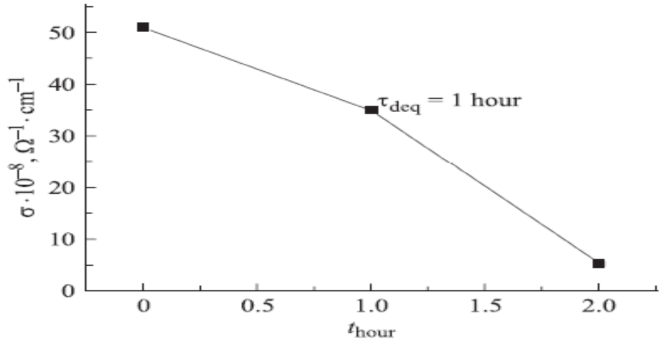

Fig. 8. Conductivity vs. processing time.

4. New electrophysical methods in the processes of industrial wastewater treatment. The fourth chapter of the work describes the electrophysical methods used to treat industrial wastewater from textile, leather, oil refineries, and soap workshops. Based on the results obtained, a technology was developed to purify industrial wastewater from harmful impurities on a natural adsorbent - clinoptilolite without activation and on a barrier discharge pre-activated in an electric field.

The technological scheme of the plant for treatment with wastewater adsorbents is shown in Fig. 9.

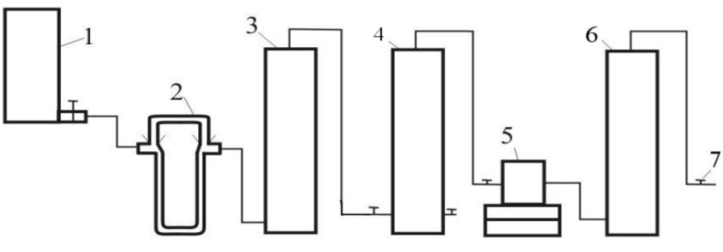

Fig. 9. Process plant diagram for wastewater treatment; 1-volume for water, 2-rheometer, 3-settler, 4-zeolite column, 5-pump, 6-container for collecting water, 7-valves.

Natural zeolite treated with an electric barrier discharge is loaded into the reactor. Electrically untreated and processed samples of natural zeolite were used in the experiments. First, wastewater of industrial production was loaded into tank 1, then a pump at a certain speed measured by remoter two was fed down the sump 3, the settled water was fed down into a special column 4, filled with an activated electric discharge adsorbent. Wastewater was passed through a zeolite column at a certain constant rate. After the adsorber, water purified by activated zeolite by pump 5 is collected in a tank 6 for collecting clean water and is discharged outside for further consumption. After each purification cycle, a water sample and a sample of the original (untreated) water, also purified by zeolite, but not activated by an electric discharge, underwent chemical analysis for the content of various impurities in them. The experimental results are shown in **Tables 2, 3 and 4.**

Table 2

Results of chemical analysis of wastewater from tanneries on a natural adsorbent activated in a barrier discharge

Indicators Waste water	Source water	Experimental conditions	
		No discharge impact	Discharge processing
pH	12,5	12,3	9
Turbidity, mg/ l	3,8	2,8	0,16
HCO_3^-,mg / l	18,4	10	0,1
Ca^{2+}, mg / l	521	401	0,1
Na_2CO_3, mg / l	10388	4536	90
$Ca(OH)_2$, mg / l	592,6	201,6	0,18
NaOH, mg / l	196	170	90
NH_4,mg / l	875	209,9	0,66
NH_4Cl, mg / l	2598,2	1234,8	2
Na_2S, mg / l	167,45	120,5	60,7

Wastewater from tanneries contains ions of chromium, copper, zinc, lead, nickel, beryllium, aluminum, iron and other metals. Chemical purification of wastewater from these impurities by treating them with alkali allows them to be purified by no more than

70%, since harmful metals are precipitated in the form of insoluble hydroxides.

Wastewater from tanneries belongs to multicomponent systems and is characterized by high concentrations of various organic and inorganic substances, which ultimately strongly pollute water resources. It can be seen from the tabular data that the wastewater treatment of a tannery contains impurities NH_4, NaOH, Ca, NH_4Cl, $Ca(OH)_2$, Na_2S, Na_2CO_3, etc. on a natural adsorbent treated in an electric field of a barrier discharge is much better (92-99%) than on untreated adsorbent (40-45%) Table 2.

The impurities in the treated water have significantly decreased compared to the original water. As a result, purified water can be used for industrial and technical purposes in a closed water supply cycle.

The fluorine content in natural water fluctuates in the range of 0.01 ÷ 12 mg / l. According to State All-Union standard RF 51232-98 "Drinking water" requirements, the maximum permissible fluoride content in drinking water is 1.5 mg / l. Therefore, the optimal concentration is considered to be about 1 mg / l.

Table 3 shows the results of experiments on the purification of groundwater from fluorine ions on clinoptilolite previously exposed to an electric discharge, decreased by 92.5%, to a value corresponding to the State All-Union standard[5] (Table 3).

Table 4 presents the results of a study of wastewater treatment of oil refineries with natural zeolite activated by a torch discharge[6]. The table shows that activating a single-phase adsorbent by a torch discharge has a significant effect on wastewater treatment. For example, when treating wastewater on an adsorbent pre-activated by a torch discharge, the amount of impurities decreases

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[5] Hasanov, M.A., Zakiyeva, I.G., Jafarova, F.Sh. Adsorptive purification of fluorine on clinoptilolite pre-treated in an electric field barrier discharge // 7-th ICTPE,- TR Northern Cyprus: - 7-9 July,- 2011,- p. 344-346.

[6] Закиева, И.Г. Изменение качественных показателей сточных вод после очистки отразличных элементов на природном адсорбенте, активированным в электрическом разряде// Баку: ELM, Журнал Проблемы Энергетики,- 2019. №4, - с. 25-30.

by 65% -90%, for oil products by 99.9% compared to water purified by an inactivated adsorbent.

Table 3

Results of chemical analysis of groundwater before and after purification from fluorine and various elements on natural adsorbent activated in a barrier discharge

No.	Name indicators	Unit measure ments	State All-Union standard2874-82	Composition of water		
				№1	№2	№3
5.	chromaticity	°C	20(35)	9	9	5
6.	Suspendedparticles	mg/ l	1,5(2,0)	3,94	2,2	0,73
7.	pH	mol / l	6-9	7,95	7	6
8.	Ammoniumsalt *(N-NH$_4$)*	mg/ l	2,0	0	0	0
9.	Hydrocarbonate (HCO_3^-)	-	-	158,6	110	170
10.	Iron (Fe)	-	0,3(1)	0,83	0,33	0,05
11.	Calcium(Ca)	-		60	5,04	5
12.	Magnesium (Mg)	mg / dm3		18,2	18,2	17,6
13.	Fluorine		1,5	4	3	0,3
14.	Mineralization(∑и)	-		448,6	426,6	422,6
15.	Soum+Potassium(Na+K)	-	200(Na)	56,8	52,1	48,5
16.	Nitrates ($NO^-{}_3$)	-	45	0,95	0,95	0,63
17.	Nitrides ($NO^-{}_2$)	-	3	0,029	0,0125	0,0035
18.	Rigidity	-	7(10)	4,02	4	3,95
19.	Carbonate hardness	mmol/L		2,6	2,6	0,5
20.	Sulfates ($SO^{2-}{}_4$)	mg/ l	500	127,3	110,5	100
21.	Dryresidue	mg/ l	1000(1500)	368	346	342
22.	Chlorides (Cl^-)	mg/ l	350	47,8	36,9	34

No. 1 - Initial water;
No. 2 - Without the impact of a barrier discharge;
No. 3 - Barrier discharge processing.

Table 4.

Results of chemical analysis of wastewater from oil refineries on natural adsorbent by activated torch discharge

No.	Name Indicators	Unit measure ments	State All-Union standard2 874-82	Composition of water		
				№1	№2	№3
2	Chromaticity	°C	20 (35)	195	175	11
3	Turbidity	mg/ l		106	79	0.8
4	pH	mol / l	6-9	6.95	6	2.8
5	Ammoniumsalt ($N-NH_4$)	mg/ l	2.0	1936	199.3	0.7
6	Hydrocarbonate (HCO_3^-)	mg/ l	-	781	781	0
7	Calcium(Ca)	mg/ l		60	60	4.5
8	Magnesium (Mg)	mg/ l		36.5	36.5	2.7
9	Mineralization ($\sum u$)	mg / dm3		4770	4748	100.5
10	Sdium+Potassium ($Na^+ + K^+$)	mg/ l	200(Na)	1183	1175	282.9
11	Nitrates (NO^-_3)	mg/ l	45	1.42	1.42	0.5
12	Rigidity	-	7(10)	6.0	6.4	2.5
13	Carbonatehardness	mmol/L		6.0	6.0	0
14	Sulfates (SO^{2-}_4)	mg/ l	500	4235	4175	103.2
15	Dryresidue	mg/ l	1000 (500)	2405	2390	100.9
16	Chlorides (Cl^-)	mg/ l	350	112	110	10.5
17	Electrical conductivity	µS	1500	6820	6800	105.9
18	Petroleumproducts	mg/ l		43111.6	284.5	5.7

No. 1 - Initial water;
No. 2 - Without the influence of a torch discharge;
No. 3 - Torch discharge treatment.

The research results formed the basis for developing a process flow diagram for industrial wastewater treatment using electric fields of various discharges.

The considered electrophysical methods of wastewater purification from various industrial enterprises showed that the best results were obtained on adsorbents treated in the electric field of a barrier discharge and the treatment of a natural adsorbent with a barrier discharge is more practical, both from an economic point of view and technology.

The developed wastewater treatment technology using an activated natural adsorbent will improve the efficiency of adsorptive treatment of industrial and domestic wastewater, thereby solving urgent problems in environmental protection.

CONCLUSIONS

1. A technique has been developed to modify a natural adsorbent's surface when exposed to corona, barrier, and torch discharges. It has been investigated and revealed that the effect of electric corona, barrier, torch discharges on a natural adsorbent leads to a charged state of the adsorbent surface [1,20].
2. It has been established that the effect of the electric field of corona, barrier and torch discharges leads to electrical charging of sorbents, improvement of their crystal structure, and purification of the entrance windows blocked by impurities in the voids of the zeolite framework, both natural zeolite and synthesized single-phase zeolite. By the method of thermally stimulated relaxation (TSR), it was revealed that the amount of accumulated charge on the surface of the natural and single-phase adsorbent is identical [12,14,20].
3. The dependence of the magnitude of the electric charge accumulated in the adsorbent on its particle size after exposure to it with a barrier discharge has been studied. It is shown that with a decrease in the particle size of the samples, the surface-treated by an electric discharge increases, which leads to an increase in the amount of charge accumulated in the adsorbent under the influence of an electric discharge [13].
4. It was found that the processing in an electric discharge of natural zeolite leads to structural changes and changes in the electrical characteristics of the composite: with an increase in the processing time, the degree of crystallinity of the adsorbent increases and, thus, the intensity of the X-ray spectra increases, and additional pores appear [22].
5. The obtained electrophysical and dielectric characteristics of composites based on activated natural zeolite confirm that the effect of an electric barrier discharge on a composite can be considered the best both from an economic point of view and taking into account the qualitative indicators of the adsorption process. [22,23].
6. It was revealed that the barrier discharge has a more significant

effect on the surface and structure of the adsorbent. Therefore, the impact of an electric barrier discharge significantly increases the adsorption capacity of adsorbents, thereby improving the efficiency of wastewater treatment of industrial enterprises, which corresponds to the values normalized by State All-Union standard RF 51232-98 [9].

7. A schematic flow diagram of an installation for wastewater treatment of industrial enterprises using a barrier discharge field has been developed and proposed, which will increase the efficiency of industrial wastewater treatment [15,17].
8. The use of this technology will increase the efficiency of industrial and domestic wastewater treatment and thereby solve a significant number of pressing problems in environmental protection. [25].

The main content of the dissertation has been reflected in the following works:

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The defense will be held on 31 May 2022, at 13^{00} at the meeting of the Dissertation Council ED 1.17 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Institute of Petrochemical Processes named after Academician Y.H. Mammadaliyev, of Azerbaijan National Academy of Sciences.

Address: AZ 1025, Baku, Khojaly avenue 30.

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Electronic version of the dissertation and abstract are available on the official website of the Institute of Petrochemical Processes of the National Academy of Sciences of Azerbaijan (www.nkpi.az)

Abstract was sent to the required addresses on 29 April 2022.

Signed for print: 26.04.2022

Paper format: A5

Volume: 36092

Number of hard copies: 20