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Nanostructured Coatings Based on Langmuir–Blodgett Films of Perfluorodecanoic Acid for Flexible Sensors for the Analysis of Lead Ions in Water

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Abstract

As a result of anthropogenic activities, the environment is polluted by heavy metals. The most important task is to find methods to control their content in water. Track-etched membranes (TeMs) can be relatively easily modified by nanometer layers of functional materials with using the Langmuir–Blodgett technique, which makes it possible to specifically change the structural, selective properties of the membrane surface and obtain new materials with desired properties. The aim of the work was to develop flexible sensors for the analysis of lead ions in water based on poly(ethylene terephthalate) (PET) TeMs with perfluorodecanoic acid (PFDA) nanolayers. Techniques for modifying TeMs based on PET with a monolayer coating based on PFDA by the Langmuir–Blodgett method, and with two-layer coatings, formed by soaking PET TeMs/PFDA in xylenol orange solutions have been developed. The microstructure and local mechanical properties of the sensor surface were studied by atomic force microscopy, and the wettability and values of the specific surface energy of PET TeMs before and after modification were evaluated using the "sessile" drop method. Based on the measurement of electrochemical characteristics, it was found that PET TeMs/PFDA have a higher response of electrochemical characteristics compared to PET TeMs and PET TeMs/PFDA/XO. The limit of detection for lead ions in aqueous solutions at pH = 12 was of 0.652 µg/l within 5 measurements.

Keywords: atomic force microscopy, flexible sensors, Langmuir–Blodgett technology, perfluorodecanoic acid

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Наноструктурированные покрытия на основе Ленгмюра–Блоджетт плёнок перфтордекановой кислоты для гибких датчиков анализа ионов свинца в воде

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В результате антропогенной деятельности в окружающую среду поступает большое количество тяжёлых металлов. Важнейшей задачей является поиск методов контроля их содержания в воде. Трековые мембраны могут быть относительно легко модифицированы нанометровыми слоями функциональных материалов с использованием метода Ленгмюра–Блоджетт, что позволяет направленно изменять структурные, селективные свойства поверхности мембран и получать новые материалы с заданными характеристиками. Цель работы – разработка гибких сенсоров на основе трековых мембран из полиэтилентерефталата с нанослоями перфтордекановой кислоты для анализа ионов свинца в воде. Разработаны методики модификации полиэтилентерефталатных трековых мембран (ПЭТФ ТМ) монослойным покрытием на основе перфтордекановой кислоты (ПФДК) методом Ленгмюра–Блоджетт, а также двухслойными покрытиями ПФДК/ксиленоловый оранжевый (КО) путём выдерживания ПЭТФ ТМ/ПФДК в растворах красителя. Методом атомно-силовой микроскопии изучена микроструктура и локальные физико-механические свойства поверхности датчиков, методом «лежащей» капли оценена смачиваемость и значения удельной поверхностной энергии ПЭТФ ТМ до и после модификации. На основании измерения вольт-амперных характеристик установлено, что ПЭТФ ТМ/ПФДК имеют более высокий отклик электрохимических характеристик по сравнению с ПЭТФ ТМ и ПЭТФ ТМ/ПФДК/КО. Предельно допустимая концентрация обнаружения ионов свинца в водных растворах при pH = 12 составила 0,652 мкг/л в пределах 5 измерений.

Ключевые слова: атомно-силовая микроскопия, гибкие датчики, технология Ленгмюра–Блоджетт, перфтордекановая кислота

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Introduction

Heavy metals are one of the main environmental pollutants. There are a number of traditional methods for detecting metal ions: atomic absorption spectrometry, mass spectrometry with inductively coupled plasma, mass spectrometry and X-ray fluorescence spectroscopy which are characterized by high sensitivity, good specificity, high accuracy, fast detection, strong interference immunity and wide linear range. However, the above methods are characterized by hardware complexity, high cost and duration. Development of new reliable and portable control methods is a promising task in the development of microelectromechanical systems.

Among sensors for monitoring of the medium, electrochemical sensors are widely used. Electrochemical analysis is portable, sensitive, and can be used to analyze metals in trace amounts. Increasing the sensitivity and selectivity is actual in the field of developing the efficiency of detecting heavy metals by electrochemical methods [1]. Performance and sensitivity of the developed sensor largely depend on the choice of suitable materials for nanocomposite sensitive layers formation.

Track-etched membranes (TeMs) have the potential to be used as universal and cost-effective flexible sensors for a variety of applications including environmental monitoring, medical diagnostics, and food safety [2, 3]. In general, choice of material for TeMs used in sensor systems depends on the specific requirements of the application, including pore size, shape, and chemical or biological function [4–8].

For example, grafting poly(4-vinylpyridine) into nanopores poly(vinylidene fluoride) (PVDF) TeMs reduces the limit of detection of mercury ions to 5 ng/l, which is much lower than the maximum allowable concentration for water [9]. PVDF TeMs modified by graft polymerization of bis[2-(methacryloyloxy)ethyl]phosphate can be used to detect uranium (detection limit of 17 ppb) [10]. Graft polymerization of methacrylic acid makes it possible to reduce the detection limit of cadmium ions by a factor of 10 compared to unmodified membranes [11]. Modified electrode of electrochemical sensors based on track poly(ethylene terephthalate) (PET) TeMs [12, 13] obtained by photograft polymerization of 2-hydroxyethyl methacrylate and subsequent formation of interpolyelectrolyte complexes with poly(allylamine), additional modification with 4-mercaptophenylbo-

ronic acid, has a detection limit of Cd (II) and Pb (II) ions of 50 $\mu\text{g/l}$ –4.25 mg/l and 10 $\mu\text{g/l}$ –4.25 mg/l, respectively. Ions of alkali and alkaline earth metals, with the exception of magnesium (up to 1 mg/l) do not affect detecting of lead and cadmium in the analyzed sample. The grafting (co)polymerization of glycidyl methacrylate and acrylonitrile (AN) with PET TeMs [14] makes it possible to obtain sensors with a detection limit of uranium up to 5.45 $\mu\text{g/l}$. Modification of membranes with copolymers with functional carboxyl and aminogroups leads to an increase in the detection accuracy of heavy metal ions due to the formation of more stable complexes. Thus, UV-induced graft copolymerization of acrylic acid and 4-vinylpyridine on PET TeMs [15] makes it possible to create sensors with detection limits of 2.22 $\mu\text{g/l}$ (Cu^{2+}), 1.05 $\mu\text{g/l}$ (Pb^{2+}), and 2.53 $\mu\text{g/l}$ (Cd^{2+}). For sensors modified with poly(4-vinylpyridine), detection limits are of 5.23 $\mu\text{g/l}$ (Cu^{2+}), 1.78 $\mu\text{g/l}$ (Pb^{2+}) and 3.64 $\mu\text{g/l}$ (Cd^{2+}) $\mu\text{g/l}$. Electrodes modified with copolymers of poly(acrylic acid) and poly(4-vinylpyridine) are sensitive at concentrations of ions Cu^{2+} – 0.74 $\mu\text{g/l}$, Pb^{2+} – 1.13 $\mu\text{g/l}$, Cd^{2+} – 2.07 $\mu\text{g/l}$.

Track-etched membranes can be relatively easily modified with nanometer layers of functional materials by the Langmuir–Blodgett (LB) method. This method makes it possible to especially change the structural properties and selectivity of the membrane surface and obtain new materials with desired characteristics. The introduction of anionic dyes into the composition of the LB-coating increases the selectivity of the separation and determination of metal cations in water. A wide range of ligands are available that can bind selectively to metal ions, including crown ethers, calixarenes, and porphyrins. These ligands can be incorporated into an organic matrix to provide a selective and sensitive metal ion sensor. For example, crown ethers are well known for their ability to selectively bind with alkali and alkaline earth metal ions [16], while porphyrins have a high affinity for transition metal ions [17]. In [18], multi-purpose mass-sensitive and electrochemical LB-multilayer sensors of dicycliclone were used to detect Cu^{2+} up to 10^{-9} M in an aqueous solution containing other analogous metal ions (Zn^{2+} and Ni^{2+}). There are research results [19] showing the possibility of using sensitive LB membranes made of poly(glutamate) containing ionophores coated with a layer of cross-linked polymer phthalocyanine-polysiloxane to determine sodium ions in aqueous solution.

Polymeric materials can also be used as a matrix material for the nanocomposite layer to provide mechanical stability and control the thickness of the layer. Polymers such as poly(ethylene glycol), poly(vinyl alcohol), and poly(acrylic acid) have been used in the formation of metal cation-sensitive nanocomposite layers [20]. In addition, quantum dots, nanoparticles (for example, gold, silver), as well as functionalized ligands sensitive to metal ions, can be included in the nanocomposite layer to increase the sensitivity and selectivity of the sensor.

The aim of the work was to develop flexible sensors for the analysis of lead ions in water based on poly(ethylene terephthalate) track-etched membranes with perfluorodecanoic acid nanolayers.

Materials and research methods

PET TeMs with pore diameters of 50 and 100 nm were used as a flexible polymer substrate. The technique for obtaining TeMs is described in [21, 22].

Nanostructured sensitive coatings on the membrane surfaces were formed by LB-method using a horizontal type of precipitation during monolayer compression achieved by the simultaneous movement of two barriers on the "Automated complex for modifying membrane surfaces with molecular and ultrathin layers". The surface pressure (π) of the film release was chosen on the basis of the experimentally obtained isotherms "surface pressure – area per molecule" in the area of the densest film layer formation ("solid film" phase state).

Monomolecular layers of perfluorodecanoic acid (PFDA, AlfaAesar) were applied from 1 mg/ml solutions in a mixture of ethyl nonafluorobutyl and ethyl nonafluoroisobutyl ethers (Novek 7200). According to PFDA compression isotherms, the "solid film" phase state corresponds to surface pressure (π) is of 5.0 mN/m (Figure 1).

The study of the structure and properties of monolayers was carried out on pre-hydrophilized single-crystal silicon wafers in a mixture of aqueous solutions of hydrogen peroxide and ammonia.

The modified TeMs were soaked in aqueous solutions of xlenol orange (XO) with a dye concentration of 0.01; 0.1 and 1 mg/ml during 10 min, 1 hour and 1 day. The samples were washed in a stream of distilled water and dried in the air.

The surface structure of the membranes was studied by atomic force microscope (AFM, NT-206, ALC "Microtestmachines", Republic of Belarus) using standard silicon cantilevers FMG 01 ("TipsNano", Russian Federation) and curvature radius no more than 10 nm.

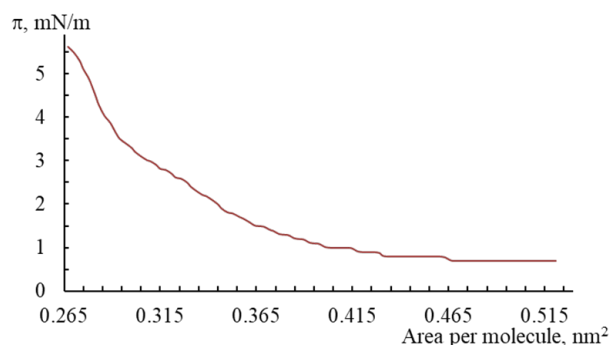


Figure 1 – Compression isotherm of perfluorodecanoic acid

The local values of elasticity modulus (E) and adhesion force (F_a) were calculated according to the Johnson–Kendell–Roberts model based on the data of the approach–retraction cantilever to the sample surface in the AFM contact mode (function "static force spectroscopy") with using cantilevers NSC 11 A (stiffness 3 N/m, Mickromash, Estonia).

The surface wettability was evaluated based on the measured values of the contact angle (CA) using DSA 100E by the "sessile" drop method using two test liquids – distilled water and diiodomethane (pure 99 %), the volume of the drops – 2 μ l. Based on the CA values, the specific free surface energy (w) was calculated by Owens–Wendt–Rabel–Kjellble method.

Sensors were made on the basis of TeMs. Gold layers 60 nm thick were deposited on both sides of TeMs by magnetron sputtering using a template (Figure 2).

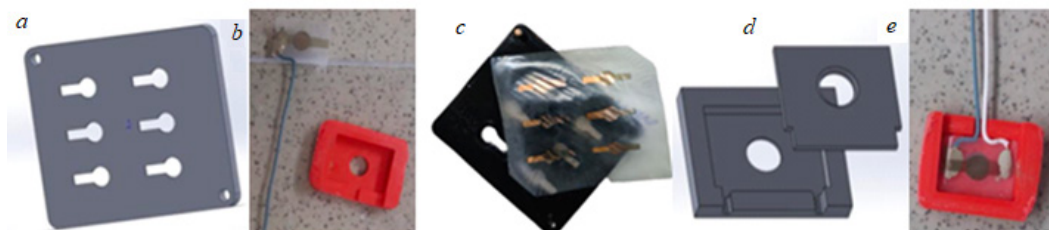


Figure 2 – Template layout for spraying (a), sensor holder (b), poly(ethylene terephthalate) track-etched membranes with a sprayed layer of gold (c), sensor holder layout (d), sensor based on poly(ethylene terephthalate) track-etched membranes (e)

Size of sensor is 5×10 mm. Connections were isolated by fingernail varnish and wax. One side of the membrane was used as working electrode, another side was used as counter electrode. These surfaces were connected to potentiostat EmStat 3 + (PalmSens) using 0.4 mm diameter copper cables with silver paste. An Ag/AgCl electrode in 3 M KCl solution was used as a reference electrode.

Calibration and determination of the sensors performance characteristics of the were carried out in solutions prepared by sequential dilution of a standard solution of lead ions (NK-EK, 10 g/ml), varying the concentration of lead ions from 0.01 mg/l to 1 mg/l. The pH of the medium in which the measurements were carried out was changed using solutions of sodium hydroxide and acetic acid.

Square wave anodic stripping voltammetry curves (SW-ASV) was performed using a standard solution of lead in an electrolyte of 0.1 M sodium acetate was performed at deposition potential of 1.2 V for 60 s, then scanning from -1 to 1 V at a frequency of 50 Hz and amplitude of 20 mV was done.

Research results

Based on AFM studies, it was shown that PFDA monolayer films on the surface of silicon wafers and PET TeMs form a uniform dense LB-layer. A number of pores on the membrane surface are closed by a modifier monolayer, the diameter of open pores decreases by 1.5–2.0 times (Figure 3). Roughness values (R_a , R_q) of modified membranes (PET-50) are reduced (Table 1).

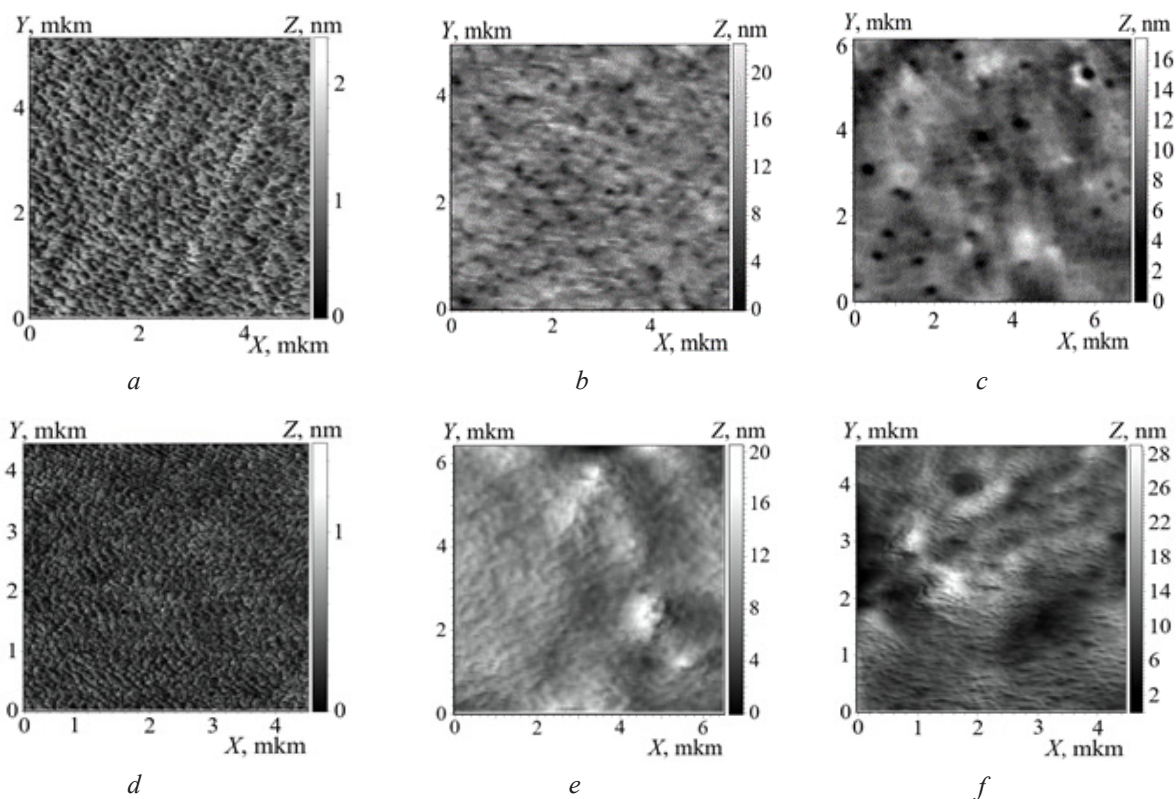


Figure 3 – Structure of initial samples of silicon (a), poly(ethylene terephthalate)-50 (b) and poly(ethylene terephthalate)-100 (c) membranes and samples modified ones with perfluorodecanoic acid Langmuir–Blodgett film (d–f)

Table 1

Roughness values of single-crystal silicon wafers and poly(ethylene terephthalate) track-etched membranes modified with a monolayer of perfluorodecanoic acid

Roughness values, nm	Si	Si/PFDA	PET-50	PET-50/PFDA	PET- 100	PET-100/PFDA
R_a	0.1	0.3	2.3	1.5	3.0	3.0
R_q	0.2	0.5	3.0	2.1	4.0	4.0

Table 2

Roughness values of poly(ethylene terephthalate) track-etched membranes/perfluorodecanoic acid/xylenol orange (soaking time – 10 min)

C (XO)	0.01 mg/ml		0.1 mg/ml		1 mg/ml	
Sample	PET-50	PET-100	PET-50	PET-100	PET-50	PET-100
R_a , nm	1.5	1.3	1.7	2.3	1.8	1.0
R_q , nm	1.9	1.7	2.2	3.0	2.4	1.3

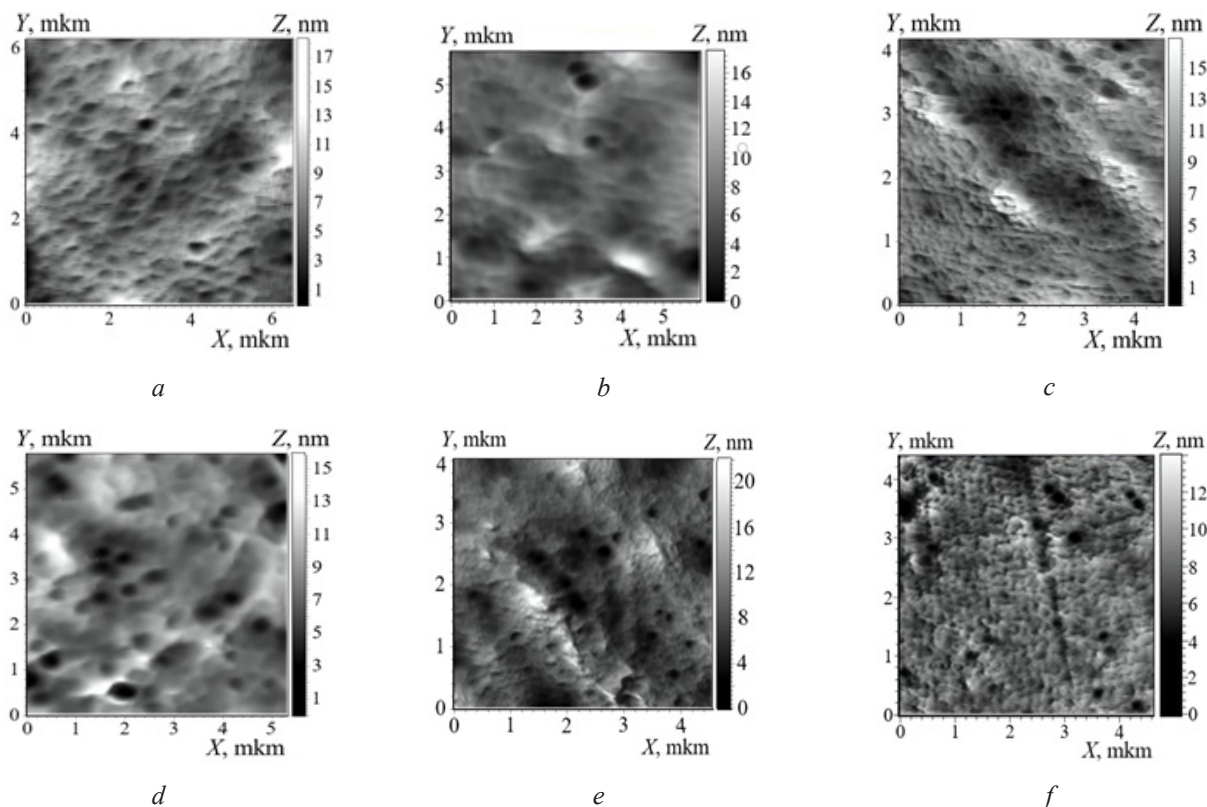


Figure 4 – Structure of poly(ethylene terephthalate)-50 (*a–c*) and poly(ethylene terephthalate)-100 (*d–f*) membranes modified with a monolayer of perfluorodecanoic acid after soaking in aqueous solutions of xylenol orange with concentrations of 0.01 M (*a, d*), 0.1 M (*b, e*), 1 M (*c, f*) during 10 min

Results of XO modification

After soaking of membrane samples with a monolayer of PFDA in XO solutions with concentrations of 0.01 mg/ml, 0.1 mg/ml and 1 mg/ml for 10 min pores on the membrane surface are "opening" (Figure 4), while the values roughness for PET-50 remains unchanged, for PET-100 are increasing significantly (Table 2) compared to membranes modified with a fluorinated fatty acid film.

The densest dye layer (according to the AFM data and the values of root-mean-square roughness R_q) was formed after exposure to an aqueous solution of XO with a concentration of 1 mg/ml.

After soaking for 1 h the pores on the membrane surface are closed, after 1 day conglomerates up to 1 μm in size are formed (Figure 5), roughness values increase for PET-100/PFDA membranes (Table 3).

Thus, the following conditions are optimal for dye adsorption: the concentration of an aqueous solution of XO is of 1 mg/ml, the soaking time is 1 h, which does not lead to desorption of monomolecular layers in aqueous solutions of dyes. The expediency of soaking in the XO solution during 1 h is confirmed by the results of the local mechanical properties of the modified samples (Figure 6).

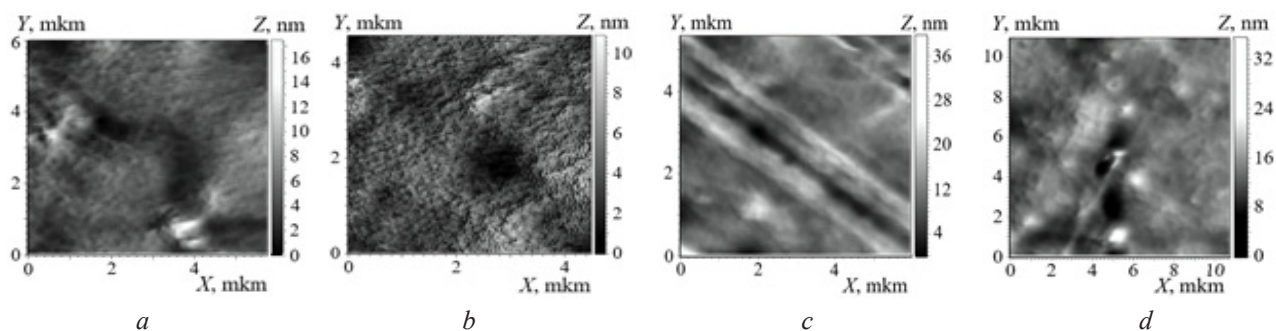
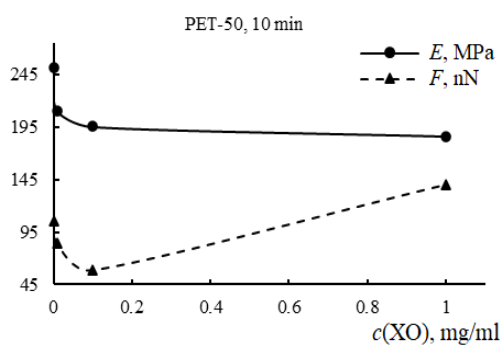


Figure 5 – Structure of poly(ethylene terephthalate)-50 (*a, b*) and poly(ethylene terephthalate)-100 (*c, d*) membranes modified with a monolayer of perfluorodecanoic acid after soaking in aqueous solutions of xylenol orange with a concentration of 1 mg/ml during 1 h (*a, c*) and 1 day (*b, d*)

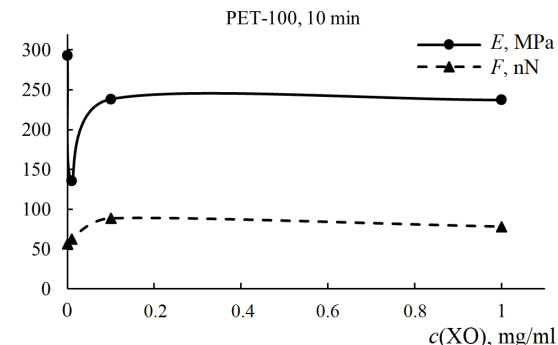
Table 3

Roughness values of poly(ethylene terephthalate) track-etched membranes/perfluorodecanoic acid/xylenol orange (concentration – 1 mg/ml, soaking time – 1 h and 1 day)

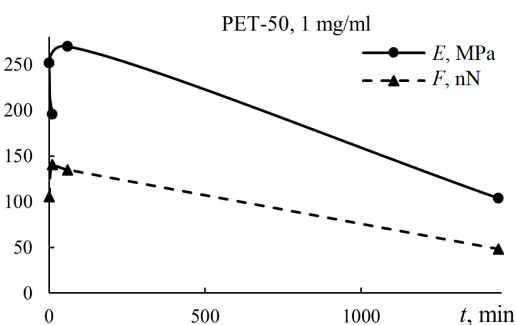
Soaking time	1 hour		1 day	
Sample	PET-50	PET-100	PET-50	PET-100
R_a , nm	1.5	2.6	1.1	1.9
R_q , nm	2.0	3.6	1.5	2.7



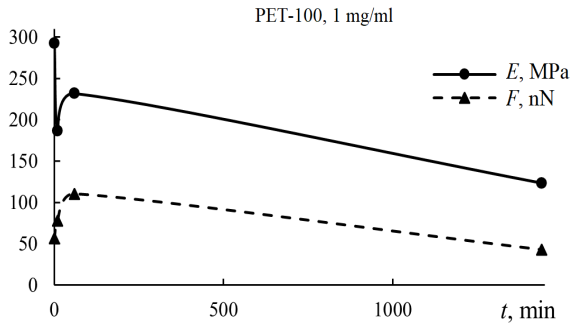
a



b



c



d

Figure 6 – Values of the elasticity modulus (E) and adhesion force (F_a) of poly(ethylene terephthalate)-50 (*a, c*) and poly(ethylene terephthalate)-100 (*b, d*) samples modified with a perfluorodecanoic acid monolayer and aged in xylenol orange solutions with a concentration of 0.01 to 1 mg/ml (*a, b*) from 10 min to 1 day (*c, d*)

The local mechanical properties of membranes modified with PFDA do not change with an increase in the dye concentration XO from 0.1 to 1.0 mg/ml. After soaking in XO during 1 day, the values of the elasticity modulus correspond to the initial values, which indicates that the acid monolayer was washed out from the membrane surface as a result of soaking in aqueous solutions of XO for a long time. An increase in the values of the elasticity modulus and a decrease in the adhesion

force of the coatings after soaking in dye solutions during 1 h are noted.

Based on the analysis of the wettability of the membrane surface, it was found that the formation of LB-films of PFDA on PET TeMs does not significantly change the wettability of the membrane surfaces (Figure 7). The values of the specific surface energy increase due to the increase in the polar component. Subsequent modification with the dye XO does not lead to significant changes in the CA.

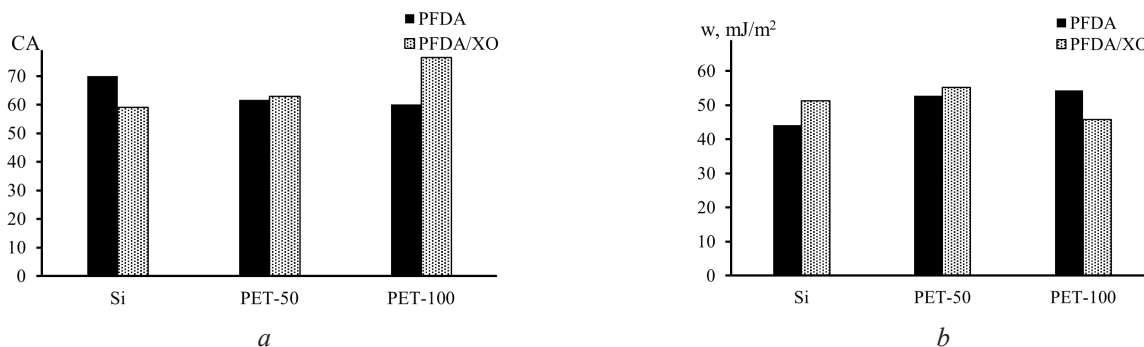
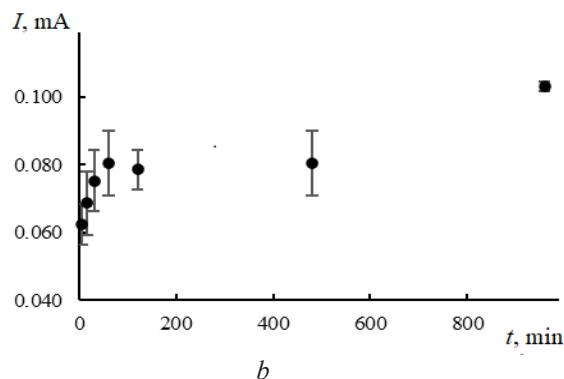
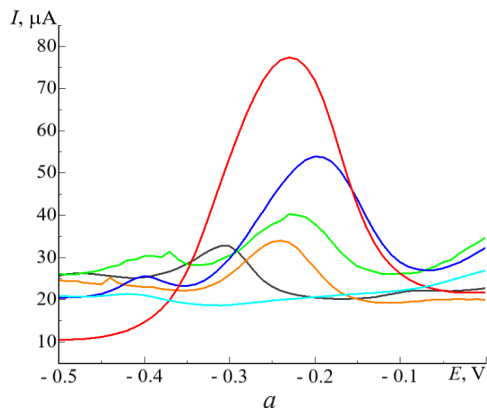


Figure 7 – Values of the contact angle (a) and specific surface energy (b) of samples of single-crystal silicon and poly(ethylene terephthalate) track-etched membranes modified ones with Langmuir–Blodgett films of perfluorodecanoic acid with xylenol orange

Results of measurement of electrochemical characteristics of sensors

Analysis of the developed sensors on the content of lead ions in aqueous solutions was carried out (Figure 8). To optimize the adsorption time and pH of the medium, sensors based on PET TeMs with a pore diameter of 100 nm were immersed in solutions with a Pb^{2+} concentration of 1 mg/l, varying the time from 5 min to 60 min. According to the results obtained, it was found that the optimal measurement time is 30 min (Figure 8b). Increasing the adsorption time of lead cations is impractical due to the fact that the values of the current strength vary within the

confidence interval. An increase in values was established with an increase in pH from 3 to 7. In the alkaline pH, there was a tendency for a slight increase in values within the confidence interval (Figure 8c), which is associated with the formation of various hydroxyl cationic forms of lead at pH from 6 up to 12. For PET TeMs modified with PFDA LB-film and PFDA/XO multilayer coating, the trend of changing electrochemical characteristics remains at different pH in solution with Pb^{2+} concentration of 1 mg/l (Figure 8c). It was found that at pH = 12 the electrochemical signal is higher compared to pH 7 (Figure 8d). Subsequent studies were carried out at pH = 12.



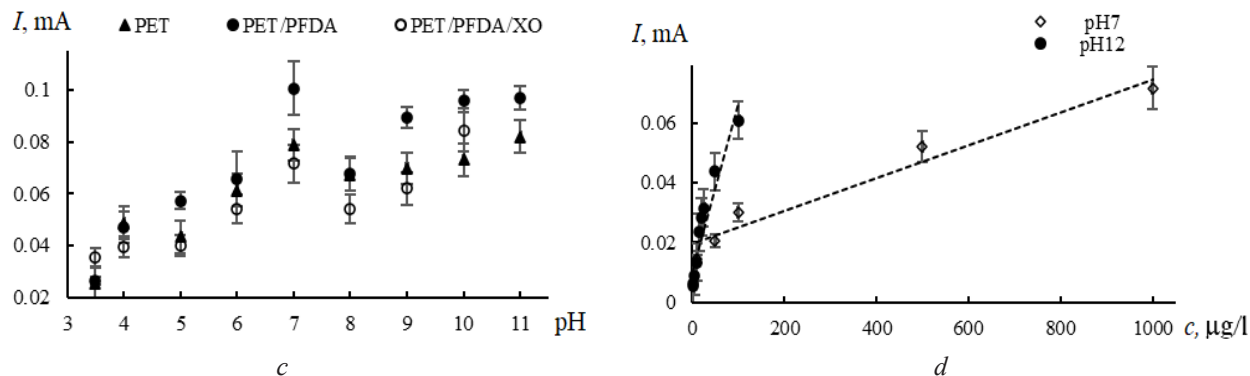


Figure 8 – Typical square wave anodic stripping voltammetry curves ($c = 0.01$ mg/l–1 mg/l, pH = (6,7–7), $t = 30$ min) (a); calibration curves of peak currents for Pb²⁺ of adsorption time based on poly(ethylene terephthalate) track-etched membranes (b); calibration curves of peak currents for Pb²⁺ of pH (c) after 30 min based of adsorption in appropriate Pb²⁺ solution in 0.1 M sodium acetate electrolyte using sensors based on poly(ethylene terephthalate) track-etched membranes and modified perfluorodecanoic acid and perfluorodecanoic acid/xylenol orange layers; effect of pH on the electrochemical signal for Pb²⁺ using sensors based on poly(ethylene terephthalate)/perfluorodecanoic acid/xylenol orange (d)

It has been shown that at pH 12 Limit of Detection concentration (LOD) of Pb²⁺ are of 397 $\mu\text{g/l}$, 0.652 $\mu\text{g/l}$, 17,7 $\mu\text{g/l}$ using sensors based on PET

TeMs, PET TeMs/PFDA, PET TeMs/PFDA/XO, consequently (Figure 9a–c). Modification of XO does not increase the sensor sensitivity (Figure 9, c).

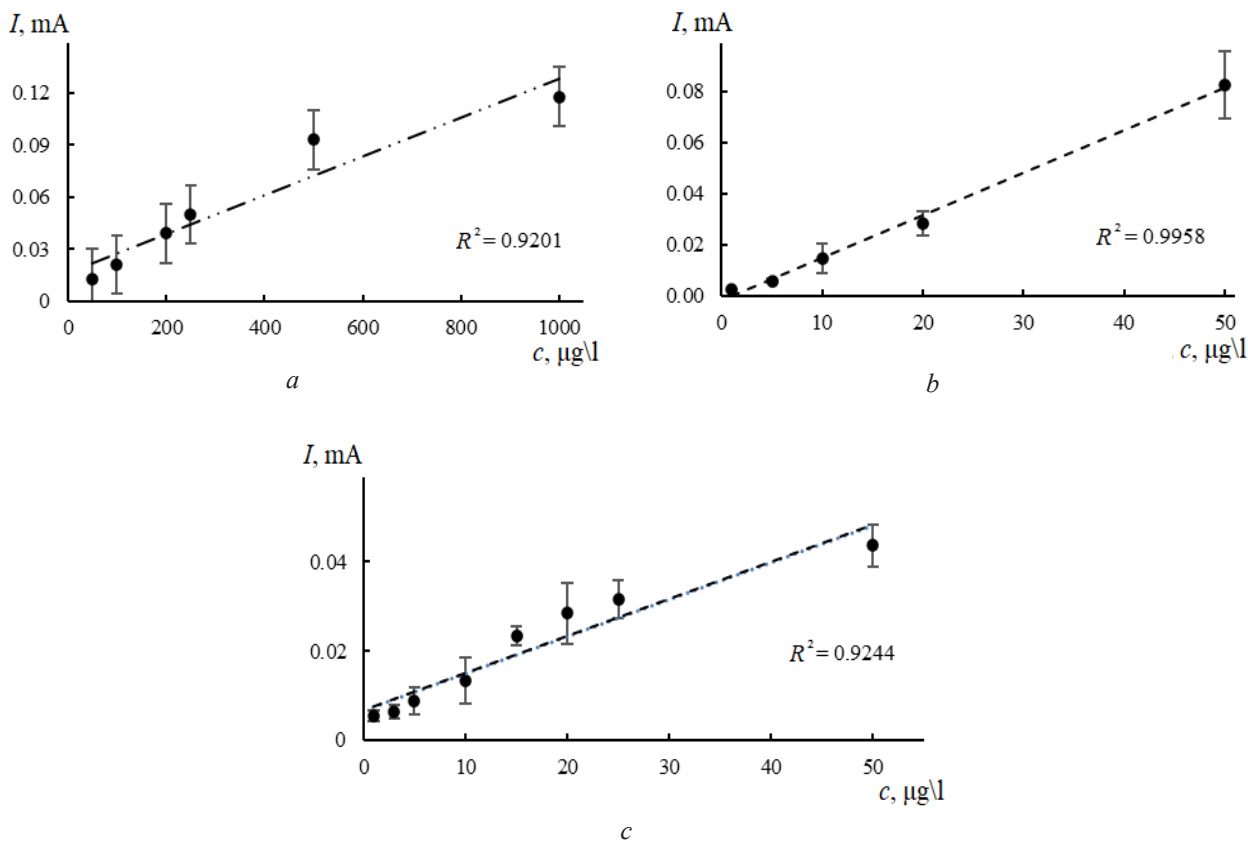


Figure 9 – Calibration curves of peak currents for Pb²⁺ after 30 min using sensors based on poly(ethylene terephthalate) track-etched membranes (a), poly(ethylene terephthalate)/perfluorodecanoic acid (b), poly(ethylene terephthalate)/perfluorodecanoic acid/xylenol orange (c)

We believe that the formation of the LB-layer of PFDA makes it possible to create a sensor for determining lead ions in aqueous solutions at pH = 12.

Conclusion

Structure of the original poly(ethylene terephthalate) track-etched membranes and the membranes modified with perfluorodecanoic acid and perfluorodecanoic acid/xylene orange coating was studied by atomic force microscopy. Determined that as a result of the modification of track-etched membranes with a pore diameter of 50 nm by the Langmuir–Blodgett layer of perfluorodecanoic acid, the roughness of the surface decreases, which indicates a uniform distribution of the modifier film over the membrane surface. In the case of membranes with a pore diameter of 100 nm, the pore size is reduced by 1.5–2.0 times. Wettability of the track-etched membranes surface changes insignificantly. It is shown that the optimal conditions for the formation of the second layer of the modifier (xylene orange) are concentration of an aqueous solution is of 1 mg/ml, the soaking time in the solution – 1 h.

Based on the results of measuring the electrochemical characteristics, it was found that the developed flexible sensors based on poly(ethylene terephthalate) track-etched membranes with a sensitive Langmuir–Blodgett layer of perfluorodecanoic acid have the highest response among all types of samples studied, the limit of detection for lead ions in aqueous solutions at pH = 12 was 0.652 µg/l within 5 measurements.

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