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ELECTROCHEMICALLY CONTROLLED SORPTION PROCESSES ON CARBON ELECTRODES

The brief overview of results obtained on electrochemical control in adsorption phenomena on carbon electrodes presented. As the examples, adsorption of phenol, benzoic acid and chloroform on the fixed flow-through beds of granulated and fiber carbon materials studied. The ability of surface charge control on electrochemically controlled adsorption phenomena is shown both from the choice of material and application of current. Polarization profiles of 3D-carbon electrodes measured. Characteristics of power consumption during electrochemical regeneration are determined. Laboratory scale experiments on water purification have shown the problems of electrochemical regeneration due to the accumulation of sorbate in the microporous structure of adsorbent.

One of the ways to control adsorption and ion exchange of substances of different nature (ionic or molecular) on carbon materials is changing the structure of interfacial double electric layer (DL), or, in other words, changing the sign and value of interface charge. The surface of sorption electrode acts as a capacitor. According to Frumkin [1], the adsorption of negatively charged species preferably takes place, on the positive charged electrode surface, while on the negative charged surface the adsorption of positively charged ones occurs. In the area of the zero charge potential (ζ_{cp}) the species of molecular structure are mainly adsorbed. In this way, at the formation of needed surface charge or at application of electric current, the electrochemically controlled adsorption or *electrosorption* takes place.

The phenomena electrosorption were studied practically completely on the surface of metal electrodes [1]. The changes in surface tension correlate with energy dissipation upon the act of adsorption. The place of electrosorption in the field of parametric pumping is well defined [2, 3]. The couple of theoretical models and experimental data dealing with these processes exist [4—7]. Still the problem is constantly under consideration [8—11].

Situation is more complicated on carbon electrode, where not only the semiconductivity of the carbon body is to be taken into account [12] but, as it shown by Soffer et al. [4], even the changes in dimensions of disperse carbon electrode. This property, in turn, could be utilized, for example, in design of artificial muscles [13].

Electrochemically controlled adsorption on carbon materials can be operated in two ways, namely from the synthesis of the prescheduled carbon material and from the application of polarizing current.

The volume of investigation of porous structure on electrosorption processes is quite sufficient [14—18]. It was shown [15] that the sorbents with $250 < S_{sp} < 450 \text{ m}^2 \cdot \text{g}^{-1}$ and with average pore radii more then 5 nM are most efficient in electrosorption processes. Such materials combine the sufficient adsorption capacity with high electrosorption reversibility. The depth of porous electrode polarization has been investigated with potentiodynamic impulse technique [16]. It was shown that the part of working surface on micro- and mezoporous sorbents depends on potential sweep rate. In the range from 0.04 up to $5 \text{ mV} \cdot \text{s}^{-1}$ the internal surface of mezoporous sorbents can be used completely without any influence of granulometric composition of carbon material. For full penetration into the internal surface of microporous carbon electrode it is necessary to keep very small potential sweep rate. Moreover, it depends also on granule size of carbon material [17].

Some limitations exist in the processes of porous carbon materials polarization, and therefore the efficiency of such electrodes decrease. One of these limitations is impossibility of DL formation in microprobes. The efficiency of regeneration process is also determined by porous structure of carbon adsorbent. According to [18], the electrochemical regeneration is possible for mezoporous adsorbents only.

The electrosorption processes have been investigated in the application to some organic compounds, such as aliphatic and aromatic alcohols [18–20], dyes [8], organic acids [19]. It was shown for the extraction of aliphatic alcohols on mezoporous carbon adsorbent under conditions of whole adsorbent surface accessibility [18] that adsorption maximum was reached in the region of own carbon stationary potential E_{st} , and adsorption value reduced on anodic or cathodic potential shift. The maximum efficiency for samples with surface values of 200–400 $m^2 \cdot g^{-1}$ and pore radii of 5–10 nM was confirmed.

At studies of the dependence of aromatic alcohol adsorption–desorption on polarizing potential at graphite surface [18] the influence of material structure on adsorption, as well as competitive electrolyte molecules adsorption was discussed. It was concluded that reversion of electrodes polarity could be used in the regeneration of adsorbent and obtaining of concentrated solutions.

Some unusual results were obtained in [20] for electrosorption of phenol, *p*-aminophenol and *p*-nitrophenol on the fibers based on pyrolyzed polyacrylonitrile (PAN). Even on microporous samples of PAN the complete desorption was possible, while on the samples produced from hydrated cellulose it took place only partially.

In spite of a large volume of studies in this field the structure of carbon body solution interface with the reference to electrochemically controlled adsorption was not taken into account. Therefore, studies of material design for electrosorption are quite rare [12, 21, 22]. Problems of the influence of the material surface charge and of the adequacy of applied potential to its real value inside the bed of material in electrosorption processes are quite unclear. Therefore, the aims of present work consisted in: determination the influence of the surface charge of carbon body on its sorption properties; measurement of potential profiles of 3D-carbon electrosorption electrode to ensure the influence of polarization; determination of the influence of porous structure on electrosorption characteristics during the cyclic process of adsorption — electrochemical regeneration of material. The main goal was to show the state-of-art in electrosorption studies and trends in technolo-

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Structure sorption characteristics of studied samples

Sample	V_s , benzene	Sorption of MB, $Mg \cdot g^{-1}$	S_{mi}	S_{me}	S_{ma}	S_{total}
8–23 Fiber ¹	0.36	320	651	31.1	0.005	682
4–97 Fiber ¹	0.42	310	225	405	1.125	682
9–186 Fiber ¹	0.83	520	468	450	0.45	918
SCS granules ²	0.70	250	750	100	1.20	850
SCN granules ²	0.71	250	770	90	0.56	860

C o m m e n t. S_{ma} — specific surface area of macropores, S_{me} — mezopores, S_{mi} — micropores, S_{total} — carbon material, $m^2 \cdot g^{-1}$; MB — Methylene Blue; ¹ Institute of Material Sciences NAS Ukraine; ² Institute of Sorption and Endoecology NAS Ukraine.

gical application of the process.

The studies of electrochemically controlled adsorption–desorption processes of some organic molecules in the fixed and dynamic beds of different carbon materials were carried out.

The fiber and granulated carbon materials, obtained from the Institute of Material Sciences NAS Ukraine, and the Institute of Sorption and Endoecology NAS Ukraine were used as sorption electrodes. Their characteristics obtained by Hg porosimetry and sorption methods are shown in the table 1.

Prior to experiment, the materials were washed in boiling ultra pure water to remove air from porous structure and than rapidly placed into the cell. The samples of granulated carbon SCN were also oxidized in the boiling 5 % solution of HNO_3 (20 volumes for 1 volume of material) during 1.5 h. All the experimental data on adsorption are shown for equilibrating times no less than 120 min.

The electrochemical measurements were held in the electrochemical cell shown in fig. 1. The cell consisted of two coaxial compartments divided by porous separator. The working space of 30 mm diameter had the Platinum mesh current collector in the bottom. It was placed onto the current flow predistributor. Platinum counter electrode was used. It was placed in the upper part of the cell behind the porous separator.

The bed of carbon granules or carbon fiber sheets was placed onto the current collector. The mesh packet was additionally pressed with plastic ring for better contact. The ring was attached clo-

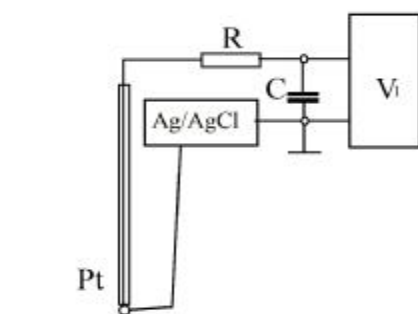
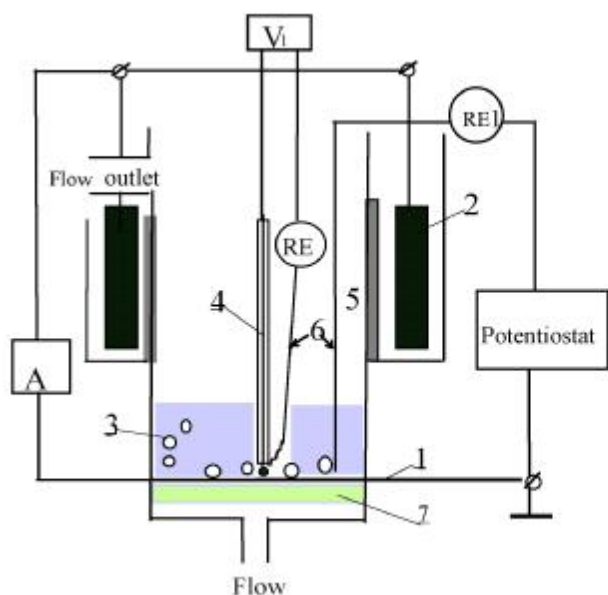


Fig. 1. Electroadsorption cell design: 1 — current collector; 2 — counter electrode; 3 — the bed of electroadsorption material; 4 — composite probe; 5 — separator of electrode spaces; 6 — Luggin capillaries; 7 — flow pre-distributor; A — ammeter of the potentiostat circuit; V_1 — independent multimeter; V_2 — voltmeter of the potentiostat. RE1 — reference electrode of the potentiostat; RE — reference electrode of the composite probe. Separately the circuit of *T*-Integrator Bridge is shown (right).

sely to the wall of working compartment of the cell.

The measurements of electrode potentials for carbon materials were made by two independent sources. The first was the voltmeter of the potentiostat PI-50-1 connected to the current collector and Luggin capillary of the Ag/AgCl reference electrode, RE1, near the surface of current collector.

The second source was the composite probe, which could move inside of the bed by means of micrometric screw. The composite probe consisted of the small Platinum sphere welded to insulated Platinum wire. The Luggin capillary with Ag/AgCl reference electrode RE was placed near to the surface of the sphere. In this case the polarizing current was applied from the potentiostat on 3-electrode circuit with the control of working electrode by RE 1. Such method was used successfully in measurements of electrode potential of solid phase in porous and fluidized bed electrodes [23—26]. The mode of measurements allows to avoid ohmic drops inside of 3-dimensional electrode and to obtain pure values of electrode potential.

To obtain average values of electrode potential the *T*-integrator bridge was used in the input chain of voltmeter V_1 analogously to [25]. Its time constant was $\tau=RC=1$ s ($R=1$ mOhm, $C=1$ microfarad).

All the electrode potential values are given in the scale of Hydrogen electrode.

The benzoic acid, phenol and chloroform were under consideration. Their dilute solutions were prepared of the chemical purity grade reagents on

ultra pure water in the presence of strong background electrolyte — 0.007 M Na_2SO_4 of different pH. The pH value of solutions in desired range was maintained by means of 0.1 N solutions of H_2SO_4 or NaOH.

The residual concentration of sorbates was measured on standard methodic with Pye Unicam PU 8800 UVVis Spectrophotometer. The 4-aminoantipyrine was added for measurements in the case of phenol and chlorophenol, and pyridine in the case of chlorophorm.

The influence of surface charge on adsorption.

To show the influence of the surface charge of carbon material the adsorption of a weak electrolyte was studied. Despite of multiplicity of studied influences on adsorption act, such as a magnitude of a free energy [16—18], change of activity of functional groups [6], influence of porous structure of a material and particulate size [17], a competitive adsorption of a weak electrolyte in its molecular and ionized forms [16—18], the electrical charge of a material surface was not considered. As we have shown recently [12], the surface charge of carbon material may be set at the stage of its preparation. This allows us to consider the adsorption of a weak electrolyte in the terms of change of a carbon surface charge.

The SCSTM and SCNTM charcoals (containing N in amounts up to 2 %) and their oxidized forms were studied in sorption of weak electrolyte. The benzoic acid (BA) was used as the sorbate. It is known [6], that BA is sorbed on carbon materials mainly in the molecular form and its $pK_a=4.2$.

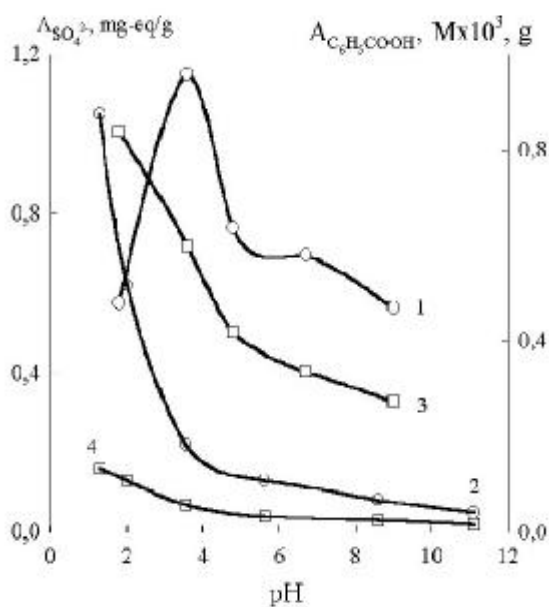


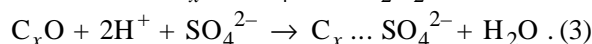
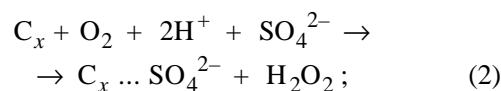
Fig. 2. The dependence of the adsorption of the weak electrolyte – benzoic acid (BA) in the bed of granulated carbon SCSTM and its oxidized form, SCS₀, on pH of the solution: 1 — adsorption of BA on SCS; 2 — adsorption SO₄²⁻ on SCS; 3 — adsorption of BA on SCS₀; 4 — adsorption SO₄²⁻ on SCS₀. Electrolyte composition: Benzoic acid (BA) — 0.007, Na₂SO₄ — 0.1 M.

The adsorption BA on active charcoal SCS and its oxidized form SCS₀ as the function of the solution pH is shown in a fig. 2. The values of adsorption of the strong electrolyte SO₄²⁻ are also shown here. It is visible, that on starting charcoal SCS the capacity on BA is small in the field of small pH and passes through the maximum laying in the area of pK_a BA (curve 1). The adsorption of a strong electrolyte is smoothly diminished with pH increase. On oxidized carbon, the adsorption of BA increases with diminishing of pH (curve 3), and the adsorption of the strong electrolyte is inappreciable (curve 4). The obtained data are similar for all charcoals studied; quantitative features of the adsorption of BA differ at the value dependent on the surface area of different carbon materials.

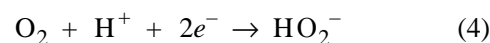
The competitive adsorption of weak and strong electrolytes is obvious. Its nature can be explained taking into account the surface charge of the material. This charge results from the oxygen chemisorption on the surface [1], when the DL is formed. The surface equilibrium is characterized by a stationary electrode potential E_{st} and is defined [1] as:

$$E_{st} = E_0 - 0.0591\text{pH} - 0.0295\lg a(\text{H}_2\text{O}_2) + 0.0295\lg P(\text{O}_2). \quad (1)$$

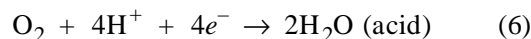
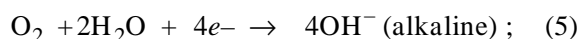
The ion exchange on the carbon surface may thus occur in two steps depending on the quantity of oxygen chemisorbed [1]:



From eqns. (2)—(3) it comes that the first stage of oxygen chemisorption with consumption of 2 electrons per Mol of oxygen



yields on changing pH the isoelectric shift of potential $\partial E/\partial \text{pH} = -29.5 \text{ mV/pH}$, while in the complete chemisorption act with the consumption of 4 electrons



the isoelectric shift value is of -59 mV/pH . Therefore, at the surface of materials with weak electron donor ability the oxygen chemisorption runs only over the first stage and yields generation of mainly some superoxide species. The same on the surface with pronounced electron donor ability forms mainly OH⁻ groups.

Therefore, the isoelectric shifts of electrode potentials of granulated carbon materials were studied after [11, 27]. Obtained data are enlisted in the table 2. The value of pzc obtained in [9, 11, 27] in inert media, when after [1] the DL is not formed, were taken into account. The positional relationship of zcp and E_{st} allows determining the surface charge of different carbons (fig. 3). If $\Delta E = E_{st} - E_{zcp} > 0$ (positive), the surface char-

T a b l e 2

The electrochemical parameters of granulated carbon materials studied

Type of charcoal	A _{BA} at pH 4, mg-eq·g ⁻¹	zcp, V	E _{st} , V	∂E/∂pH, mV
		pH		
SCN (N=2 %)	1.56	-0.08	0.48	46
SCN ₀	0.44	0.49	0.45	29
SCS	1.22	0.10	0.38	47
SCS ₀	0.28	0.58	0.37	29

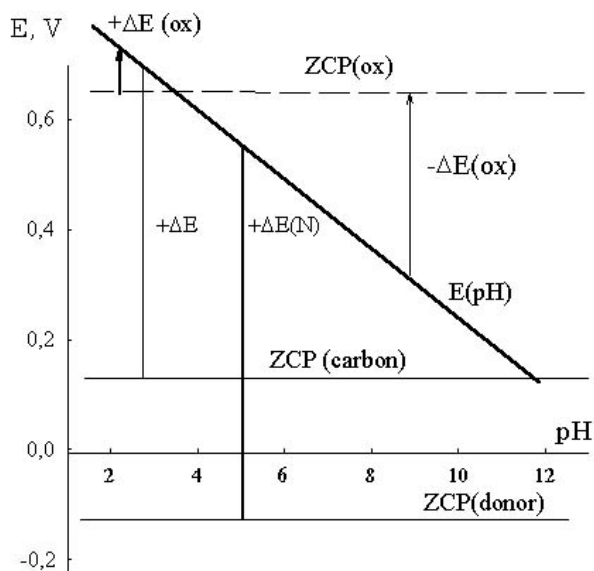


Fig. 3. The diagram of the surface charge formation for carbon material in oxygen containing electrolyte [10].

ge is positive and adsorption of anions takes place on the surface; in opposite, if $\Delta E < 0$ (negative), the adsorption of cations takes place. The $\Delta E = 0$ means zcp point. The value of ΔE gives initial information on adsorption capacity of the material.

It comes from table 2 that the presence of heteroatom-donor N the zcp value shifts towards cathodic potentials, while in presence of heteroatom-acceptor, =O on oxidation the isoelectric shift lowers down to -30 mV indicating the lowering of the ability to chemisorb oxygen. The correlation of E_{st} and zcp values for relevant initial and oxidized materials gives the information on the interfacial charge of charcoals (fig. 3).

The adsorption of a strong electrolyte increases with the increase of this charge for the charcoal with the positive surface charge. Accordingly, BA, as the weak acid, is sorbed in the molecular form in the area of neutral pH. Below pH 4 its dissociation is suppressed, and the adsorption of the strong acid becomes more preferable. In contrary, for oxidized charcoal, in which the surface charge is small and changes the sign in the area of $3 < \text{pH} < 4$, the adsorption of a strong electrolyte is suppressed, and in the area close to pzc the partially dissociated substance is sorbed.

The difference of the values of BA adsorption on pure carbon charcoal SCS and N-containing charcoal SCN is mirroring the role of heteroatom-donor in adsorption of BA.

Thus, on the particular example the influence of the surface charge of charcoal on the adsorption of a weak electrolyte was shown. Observed phenomenon gives the opportunity to control the adsorption rate by means of forming the electrode potential of carbon material.

The behavior of the carbon bed under polarization. Usually the application of electrosorption using carbon electrodes is considered as not enough efficient [3]. It was supposed to be connected to the non-uniform potential distribution within the bed of carbon material. Therefore, polarization profiles in the bed of carbon fibers were measured with the composite probe (fig. 1). They are shown in fig. 4. Obtained potential profiles look similarly to the same in the fixed or fluidized beds of carbon granules [27]. They depend not only on bed porosity and conductivity. The changes of potential values in time are observed, too.

The polarization phenomena on 3D-carbon electrode differ from known for electrodes containing metallic particles, as with increasing of electrolyte conductivity the average polarization shifts not to the current collector, but to the front of the electrode. It may be caused by charging of internal micropores of carbon body, which can influence the changes in the structure of DL.

On this reason, in diluted electrolytes the application of current is unproductive. Electrode potential of the carbon bed slightly changes in time, and differs from those of current collector. Increasing the concentration of electrolyte gives the

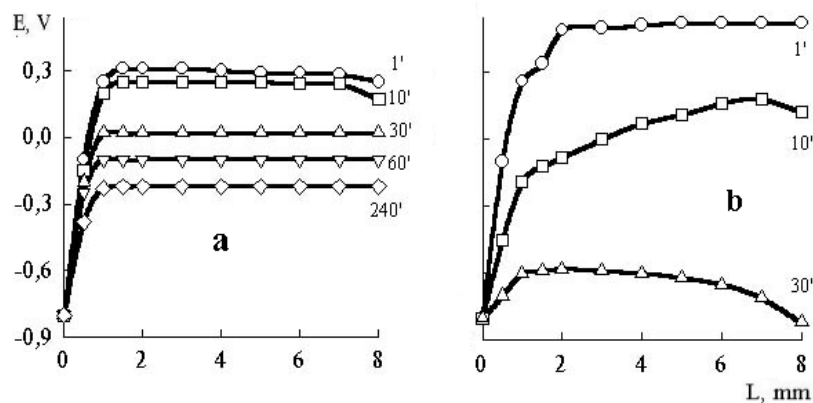


Fig. 4. Polarization profiles of carbon fiber beds (15 layers of sample № 4-97) in 0.007 M (a) and 0.08 M (b) solution of Na_2SO_4 , pH 5. Current collector is placed at $L=0$.

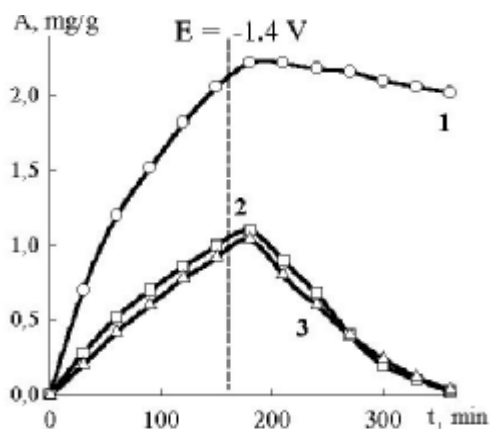


Fig. 5. Adsorption and electrodesorption of CHCl_3 at a potential of -1.4 V on microporous (1, 2) and mezoporous (3) carbon fibers. Samples: 1 — 9-186; $S_1=918 \text{ m}^2\cdot\text{g}^{-1}$; 2 — 4-97; 3 — 8-23; $S_{2,3}=682 \text{ m}^2\cdot\text{g}^{-1}$.

possibility to control the potential distribution within the bed.

The surface areas and porous structure are known to play significant role, too, in electroadsorption process. This point was checked out during electrodesorption of CHCl_3 on different carbon fiber materials. The uptake of CHCl_3 was conducted from the solution modeling drink water and containing 0.007 M solution of Na_2SO_4 , pH 5. The electrodesorption was conducted from the solution containing 0.08 M Na_2SO_4 at pH 5.

As it comes from fig. 5, carbon materials with S_{sp} of average $600 \text{ m}^2\cdot\text{g}^{-1}$ and mainly mezoporous structure are efficient in electrodesorption. On the microporous carbon material with large surface area the rate of adsorption–desorption practically cannot be controlled electrochemically.

It is also shown that the cathodic polarization is optimum for the desorption of most organic molecules. In such conditions adsorbed hydrogen atoms displace each molecule being adsorbed previously.

Power consumption during electrochemical regeneration. Polarization of the beds of carbon materials in time is determined by the sum of electrochemical processes: changing the DL structure in the porous media of carbon materials; electroreduction of dissolved oxygen; adsorption of hydrogen.

The processes of charging and Faradays processes could not be divided, as in any case two systems of current distribution exist, namely the first in the 3D bed, and the second in 3D granule media.

The dependence of current density on time in

the bed of fiber and granulated carbon materials during electrochemical regeneration is shown at figs. 6, 7. On increasing of polarizing potential the current density reaches its plateau. As the overvoltage of hydrogen evolution on carbon materials is rather high (Tafel coefficient $a = -0.9 \text{ V}$) [7], the current is mainly spent on the electroreduction of dissolved oxygen. So the current in the cell may be considered as the i_d for oxygen.

On the stationary value of i_d at the long times of polarization the working area of the carbon bed was determined for granulated carbon sample SCN^{TM} (fig. 7, curve 3) according to equation:

$$i_d = nFc_0D/\delta, \quad (7)$$

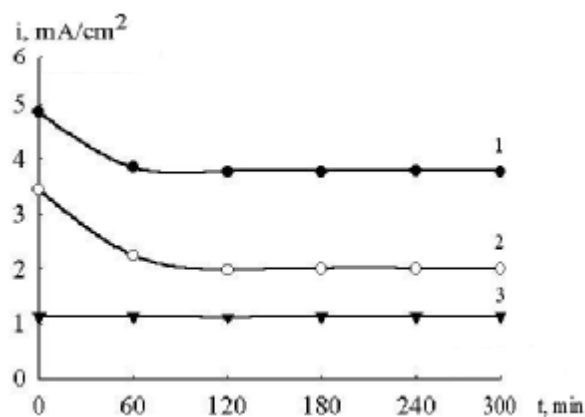


Fig. 6. Dependence of current density on time in the bed of carbon fiber material during electrochemical regeneration. Sample 4-97, 5 layers ($L=2.5 \text{ mm}$); electrolyte — Na_2SO_4 $10 \text{ g}\cdot\text{l}^{-1}$, pH 6.5. Potential of current collector, V: 1 — 0.2; 2 — 0.4; 3 — 0.8.

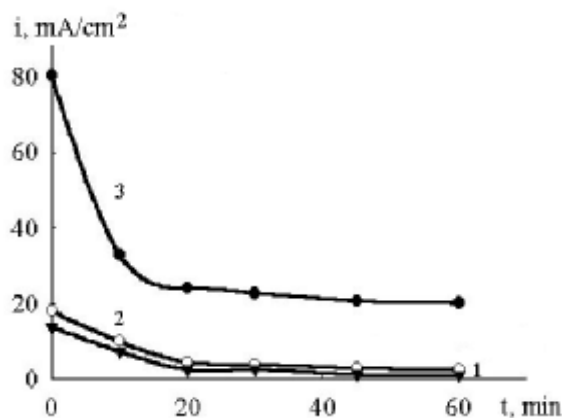


Fig. 7. Dependence of current density on time in the bed of granulated carbon material during electrochemical regeneration. Sample SCN^{TM} , $L=10 \text{ mm}$, $0.6 < d_p < 0.9 \text{ mm}$; electrolyte — Na_2SO_4 $10 \text{ g}\cdot\text{l}^{-1}$, pH 6.5. Potential of current collector, V: 1 — 0.0; 2 — 0.3; 3 — 0.6.

where i_d — diffusion current density, $\text{mA}\cdot\text{cm}^{-2}$; c_o — concentration of dissolved oxygen, $c_o=8.3\text{ mg}\cdot\text{l}^{-1}$ after [23]; diffusion coefficient, $D_{\text{ox}}=1.4\cdot 10^{-5}\text{ cm}^2\cdot\text{s}^{-1}$ [23]; thickness of diffusion layer, $\delta=1.2\cdot 10^{-3}\text{ cm}$, determined by us [24].

From the values of total current and taking into account the condition, that all the electrode area is working under diffusion current conditions [23], the effective working surface, S_{ef} was estimated. The value of $S_{\text{ef}}=44.8\text{ cm}^2\cdot\text{cm}^{-3}$.

The geometrical surface area was calculated as:

$$S = 6(1 - V)/d_p, \quad (8)$$

where V — voidage, $V=1 - V_{\text{bed}}/V_{\text{particles}}$ ($V=0.39 - 0.4$ for packed bed); d_p — average particle size, cm; $S = 46.5\text{ cm}^2\cdot\text{cm}^{-3}$, and so S_{ef} is practically equal to geometric surface.

This result shows that the part of current, spent in porous structure, is negligibly small.

It may also be seen from fig. 6 and 7, that current density on fiber materials is more then order higher then on granulated materials due to its open surface structure. This confirms the better sorption capacity of fibers compared to granules.

Laboratory scale electrosorption cell. On the basis of microkinetic measurements, the laboratory scale electrosorption cell was designed (fig. 8). Its working electrode consisted of 5—15 layers of carbon fibers, each 0.5 mm thickness. Electrode was pressed by the system of screws to the current collector 4, made of impregnated graphite MPG7,

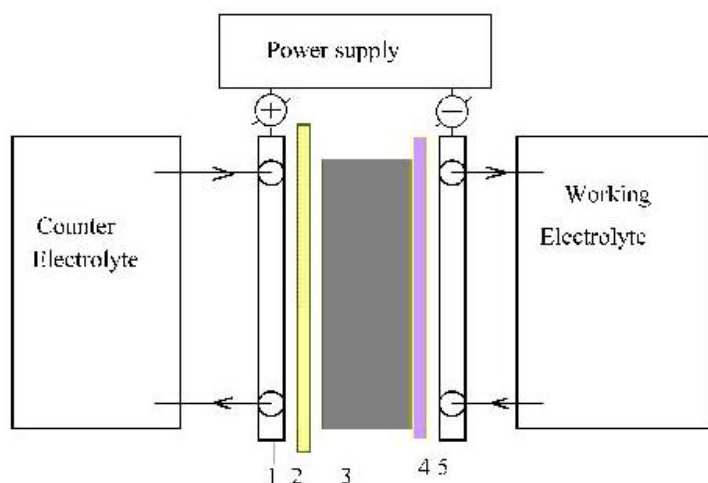


Fig. 8. Laboratory scale electrosorption cell: 1 — current collector of counter electrode; 2 — porous separator; 3 — carbon fiber material; 4 — current collector and 5 — current feeder of working electrode.

with the contact mesh, made of stainless steel X18N9T. Counter electrode is divided from working electrode by means of polypropylene fiber separator 2.

The system of inlet–outlet couples made possible to change flow directions of electrolyte. Such cell could be used in cathodic regeneration regime only. This regime is most reasonable, taking into account literature overview and experimental data, and also from the point of choice of electrode material, stable under anodic polarization. The problem of anodic passive oxide films on carbon materials thus was also avoided.

Proposed cell design is made to minimize interelectrode spaces and thus to minimize the working voltage. The single module was tested, but it could be contacted in bipolar side-by-side connection of cells, in parallel to electrolyte flow and in consequence on current flow.

Laboratory scale runs were aimed on the removal of phenol from drink water. The working electrode consisted of 5 sheets of carbon fibers (sample 4-97, dimensions of each sheet $50\times 60\text{ mm}$). The volume of treated solution modeling drink water was 200 ml. It contained av. $200\text{ mg}\cdot\text{l}^{-1}$ of NaCl and $200\text{ mg}\cdot\text{l}^{-1}$ of Na_2SO_4 . The initial concentration of phenol was $20\text{ mg}\cdot\text{l}^{-1}$. The 100 ml of electrolyte containing $10\text{ g}\cdot\text{l}^{-1}$ Na_2SO_4 was used for the regeneration. Regeneration was provided in steady state and cyclic mode; regenerate was then removed. Calculations on the rate of regeneration of sorption electrode were made by following equation:

$$R_{\text{reg}} = (m_{\text{sorb}} - m_{\text{desorb}}) \sum m_{\text{sorb}} \cdot \quad (9)$$

The data of laboratory scale runs are listed in table 2.

As it follows from the pilot runs, both sorption capacity of electrode material and the regeneration rate decrease in time. It is connected to the storing of phenol in the micropores of studied material. Only using materials with prevailing mezoporous structure can improve the process.

Adsorption of phenol, benzoic acid and chloroform on the fixed flow-through beds of granulated and fiber carbon materials studied. The capability of surface charge control on electrochemically controlled adsorption phenomena is shown. The adsorption of organic species on carbon materials can be controlled by the surface charge of the material. The needed properties of

Table 2

List of laboratory scale runs on water purification from phenol (Ph)

Run №	Quantity of sorbed Ph, mg		Quantity of desorbed and left Ph, mg		τ , h	U, V	P, Wt	Rate of, %	
	Initial	Total	De-sorbed	Left				purification	regeneration
1	2.82	2.82	2.26	0.56	0.5	2.1	0.255	70	80
2	2.53	3.09	1.08	2.01	0.5	2.0	0.24	49	35
3	3.75	5.75	1.88	3.88	0.5	2.0	0.24	57	33
4	3.72	7.60	1.67	5.93	0.5	2.0	0.24	46	22
5	3.12	9.05	1.62	7.43	0.5	2.0	0.24	27	13
6	3.33	10.76	1.00	9.76	0.5	2.0	0.255	46	9
7	3.51	13.27	0.88	12.4	0.5	2.0	0.24	29	6
8	3.57	15.96	0.82	15.14	0.5	2.0	0.24	23	5
9	3.67	18.82	0.81	18.01	0.5	2.0	0.24	23	4
10*	3.71	21.72	3.45	18.27	10	3.0	0.36	21	16
11*	2.73	21.00	1.38	19.62	30	3.0	0.36	62	6
12*	3.1	22.72	1.52	21.20	3.5	3.0	0.36	44	7

* Flow-through regime.

material can be achieved by its choice and surface treatment. Polarization profiles of 3D-carbon electrodes measured. Efficient electrodesorption is shown to be possible only in the electrolyte solutions with concentrations more than 1–5 g·l⁻¹. Characteristics of power consumption during electrochemical regeneration process determined. Electric current in electrodesorption is spent mainly on oxygen reduction reaction. Its average magnitude (15–25 mA·cm⁻² for carbon fibers) determines the power consumption for regeneration process. Laboratory scale experiments on water purification have shown the problems of electrochemical regeneration due to the accumulation of sorbate in the microporous structure of adsorbent.

РЕЗЮМЕ. Представлено короткий огляд результатів вивчення електрохімічно керованої адсорбції на вуглецевих матеріалах. Як приклади розглянуто адсорбцію фенолу, бензойної кислоти і хлороформу на проточних об'ємних волокнистих і гранульованих електродах. Виміряно профілі потенціалів об'ємних вуглецевих электродів. Показано можливість керування зарядом поверхні електрода як з боку синтезу, так і накладенням поляризації. У той же час, спроби очистки води від органічних речовин електросорбцією в циклічному режимі поглинання–регенерації наштовхну-

лися на проблему нагромадження сорбату в мікропористій структурі матеріалу.

РЕЗЮМЕ. Представлен краткий обзор результатов изучения электрохимически управляемой адсорбции на углеродных материалах. В качестве примеров рассмотрена адсорбция фенола, бензойной кислоты и хлороформа на объемных проточных волокнистых и гранулированных электродах. Измерены профили потенциалов трехмерных углеродных электродов. Показана возможность управления зарядом поверхности электрода, как со стороны синтеза, так и наложением тока. В то же время, попытки очистки воды от органических веществ электросорбцией в циклическом режиме поглощения–регенерации натолкнулись на проблему накопления сорбата в микропористой структуре материала.

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ИСПОЛЬЗОВАНИЕ ТЕОРИЙ АНАЛИЗА РАЗМЕРНОСТЕЙ И ПОДОБИЯ ДЛЯ ОПИСАНИЯ КИНЕТИКИ ЭЛЕКТРОХИМИЧЕСКИХ ПРОЦЕССОВ

Показана возможность использования теории обобщенных переменных для описания кинетики простейшей электрохимической реакции. Получены три комплексные безразмерные величины, характеризующие соответственно относительную скорость, степень нелинейности и степень необратимости электродного процесса. Путем численного моделирования установлена количественная взаимосвязь между этими комплексами для электрохимической реакции с лимитирующей стадией разряда-ионизации.

Разработка и анализ кинетических моделей электрохимических реакций представляет собой в общем случае весьма сложную задачу. Затруднения, с которыми приходится сталкиваться при решении этой проблемы, обусловлены как непростым физико-химическим содержанием процессов переноса массы и заряда через границу раздела фаз проводник 1-го рода—проводник 2-го рода, так и сложной формой соответствующего математического аппарата. Большое число разнородных переменных, вводимых для описания кинетики электрохимических реакций, зачастую затемняет общую картину явлений и не позволяет найти скрытые связи системы и объединить эти связи в простые количественные закономерности.

Однако в действительности влияние отдельных факторов, представленных разными величинами, проявляется не по отдельности, а совместно, анализируя поведение сложных систем, к числу которых можно отнести любой электрохимический процесс, следует рассматри-

вать эти величины в совокупности, объединяя их в комплексы, определяющие конечный результат воздействия ряда факторов и имеющие, таким образом, ясный физический смысл.

Данная идея лежит в основе теорий подобия и анализа размерностей (теории обобщенных переменных) [1, 2], широко используемых в различных областях науки и техники для анализа поведения самых разнообразных сложных систем и процессов. В то же время в современной электрохимии эти теории еще не находят широкого применения, хотя могут оказаться весьма полезными и плодотворными в целом ряде случаев [3, 4]. Цель нашей работы заключалась в рассмотрении возможности применения методов теории обобщенных переменных для описания кинетики простейшей электрохимической реакции.

Особенностью и достоинством данных теорий является то, что они применимы, даже если уравнения, определяющие процесс, неизвестны. В таком случае для получения комплексов, опи-

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