

Effective numbers of electrons as a characteristic of adsorption processes on perfectly polarizable electrode hemosorbents

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Abstract An investigation of electroless electrochemical detoxification processes occurring on porous hemosorbent electrodes was performed. Cupric ions, isopropanol, *t*-butanol, and free hemoglobin were used as model toxicants. The elementary act of electrochemical adsorption detoxification was shown to nearly always be accompanied by partial transfer of charge. It was concluded that the method of experimental determination of effective numbers of electrons that correspond to the elementary act of detoxification is a robust tool for the selection and evaluation of relative effectiveness of hemosorbent electrodes.

Keywords Porous carbon electrode · Partial charge transfer · Electroless electrochemical detoxification · Hemoperfusion · Hemosorption

Introduction

A variety of different materials are utilized in modern medical technologies, such as a number of metals and alloys, polymers, porous carbon materials, and composite materials. The contact of such materials, which are foreign to the human organism, with blood or other tissues can lead to a number of undesirable side effects, including blood cell trauma, adsorption of proteins on the surface of the foreign material, blood clot formation (thrombogenesis), and other interactions that can lead to complications or prohibit their medical use. When foreign materials that conduct electricity come in contact with human blood or tissue, they can be considered as electrodes immersed in 0.15 M solution of sodium chloride. The occurrence of destructive electrochemical processes on such electrodes on contact with blood or tissue is especially dangerous—both in the case of long-term implants such as cava filters, stents, or endoprosthetic devices and short-term contact of the material with blood, as in hemoperfusion treatment [1, 2].

One of the most important potential applications of electrochemical technologies in medicine is the electroless hemoperfusion (hemosorption) detoxification, which removes exo- and endotoxins from the organism. A detailed analysis of the interaction of porous carbon-based hemosorbents with blood [2] has shown that the interaction with blood cells and proteins depends on the carbon potential and is related to the sign and magnitude of charges

The authors extend their best wishes to Professor Waldfried Plieth as he celebrates his birthday! One of the authors (BMG) has warmest memories of his time spent at Technische Universität Dresden with Professor Waldfried Plieth working on the development of the theory of surface tension for solid electrodes.

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localized at the membranes of blood cells and on the surface of the carbon material immersed in blood or another biological medium. This electrochemical model has not only led to the elucidation of the causes of blood trauma but it has also resulted in a number of technological solutions being proposed to prevent such trauma in the course of hemoperfusion. Thus, it was shown that the electrochemical mechanism underlies the interaction between blood components and the surface of carbon materials, leading to the development of an electrochemically controlled hemosorption detoxification method.

The synthesis of new hemosorbents from carbon or composite materials [3] implies both an investigation of their adsorption properties toward the chosen class of toxicants and of their activity toward blood cells and proteins [2]. Such data are crucial for proper selection of prospective hemosorbents, since the occurrence of electrochemical processes on electrodes made of carbon materials in the course of adsorption from biological media can lead to protein denaturation on the sorbent surface. Such processes have been observed on the platinum electrode [4], with a layer of denatured proteins being formed on the platinum surface as a result.

It can be supposed that, if the amount of charge transferred between the substrate and the hemosorbent electrode in an elementary act of adsorption can be determined [5], the obtained value of the effective number of electrons could be used to elucidate the mechanism of interaction of the biological medium with the porous-carbon hemosorbent and, therefore, to predict the suitability of new hemosorbent materials for safe contact with the medium. In regard to this, it should be emphasized that activated carbon must be viewed as a perfectly polarizable electrode whose state is wholly dependent on its total charge [6]. This does not imply any relationship between the total charge and the free charges on either side of the electrode surface.

The primary goal of the present work is to experimentally determine the effective number of electrons for the investigation of the adsorption of isopropanol, *t*-butanol, and cupric ions as model organic and inorganic toxicants, respectively, on AG-3 activated carbon. The theory of effective charge transfer is also applied to plasmosorbent electrodes made of activated carbons modified with conductive polymers containing various dopants in the course of their interaction with complex protein molecules. The present work makes use of Frumkin's idea regarding the predominant role of the electrochemical mechanism in adsorption processes on activated carbons [7].

The model toxicants chosen for the experiments differ in their chemical properties as well as their severity and mechanism of toxic action. Isopropanol has a narcotic action and is metabolized to acetone that can accumulate in the

organism in large amounts. *t*-Butanol is potentially much more toxic than lower-mass homologs and can lead to narcotic intoxication and death in animals. Heavy metal toxicity is primarily due to their reactivity toward proteins in the tissue, resulting in denaturation of proteins and the formation of metallic albuminates, or metal protein salts. In cases where only superficial tissue strata are involved in such denaturation, a reversible astringent or irritating effect is produced; on the contrary, if profound denaturation occurs affecting a large number of cells in the tissue, a cauterizing effect arises, resulting in irreversible changes to the affected tissue, i.e., necrosis. Cupric ion poisonings most frequently occur as a result of direct contact with copper sulfate solutions [8], for instance when used as a pesticide.

Chemically, cupric ions are good oxidizing agents, as they can be easily reduced to metallic copper, while isopropanol can be oxidized to acetone and *t*-butanol cannot be oxidized (both alcohols are not easily reduced *in vivo*). This is important, since the mechanism of interaction between the adsorbate and the hemosorbent electrode depends partly on the nature of the adsorbate.

Theory

The seminal work on the theory of adsorption of surface-active substances was published by Frumkin in 1926 [9] where a linear dependence was shown between the charge of a perfectly polarizable electrode q and its coverage with a surface-active adsorbate. This dependence can be expressed as follows in Eq. (1):

$$q = q_0(E) + q_1(E)\Gamma \quad (1)$$

where Γ is the Gibbs' surface excess (adsorption) of a surface-active substance and $q_0(E)$ and $q_1(E)$ are some functions of the electrode potential E .

The differential for Eq. (1) can be written as follows:

$$dq = CdE - nFd\Gamma \quad (2)$$

In Eq. (2), C denotes the capacitance of a perfectly polarizable electrode when the coverage degree of its surface with a surface-active substance is constant [10], F denotes Faraday's constant, and n denotes the effective number of electrons that characterizes the elementary act of adsorption of surface-active substance molecules:

$$n = -F^1(\partial q/\partial \Gamma)_E \quad (3)$$

In an electroless regime (i.e., in an open-circuit experiment), the left side of Eq. (2) is equal to zero, giving us a very important characteristic of the hemosorbent electrode,

which comprises the ratio of its capacitance to the effective number of electrons:

$$C/n = Fd\Gamma/dE \tag{4}$$

The expression on the right side in Eq. (4) can be determined experimentally. The value of capacitance C can also be determined from experimental data. Therefore, Eq. (5) can be used:

$$n = F^{-1}CdE/d\Gamma \tag{5}$$

for experimental determination of the effective number of electrons n , which characterizes the elementary act of the adsorption process on the hemisorbent. It should be noted that the derivative $(\partial/\partial\Gamma)_E$ has also been utilized in the theory of electrochemical redox reactions that include an adsorption step [11].

In real experimental conditions, the differentials $d\Gamma$ and dE must of necessity be replaced with the finite decrements $\Delta\Gamma$ and ΔE . Therefore, the following equations were used for computations with experimental data:

$$C/n = F\Delta\Gamma/\Delta E \tag{6}$$

$$n = F^{-1}C\Delta E/\Delta\Gamma \tag{7}$$

Equations (6) and (7) were used for calculations of the ratio of electrode capacitance to the effective number of electrons and the effective number of electrons, respectively. It is noteworthy that both of these characteristics of a hemisorbent depend on its potential [8, 9].

Experimental

Electrochemical measurements were performed on an IPC-Pro L potentiostat (NTF Volta, Ltd., Russia), with potentials measured against a saturated silver/silver chloride electrode; 0.20-M aqueous solutions of sodium sulfate were used as

the background electrolyte. Experiments were performed on AG-3, SKT-6A, and VSK-A (NPO Neorganika, Russia). Electrochemical modification of carbon samples to potential values in the range between -910 and +475 mV was carried out according to the electrochemical method described in [2, 12] by constant potential polarization. Open-circuit potentials of carbon were measured in a cell described in [12] and correlated with the extent of modification, which was controlled by varying the applied constant potential, the quantity of electricity passed through the carbon while in the modification electrolyzer and the concentration and composition of the electrolyte used for modification in a way similar to that described in [12]. Modified and unmodified samples of activated carbons were then used for the synthesis of composite materials used as model plasmosorbents for the removal of free hemoglobin (Hb); electropolymerization of pyrrole on activated carbon samples [13] and adsorption of cupric ions from an aqueous solution in an open circuit were used to obtain these composite materials.

The concentration of alcohol toxicants (*t*-butanol and isopropanol) in solution was determined by gas chromatography on an SRI 310C chromatograph equipped with a TCD detector (SRI Instruments, USA). Cupric ion concentration was measured spectrometrically on a Genesys 10uv (Thermo Scientific, USA) and a DU 800 (Beckman-Coulter, USA) scanning spectrophotometers at λ_{max} values of 808 and 607 nm (as a ammonia complex), respectively.

The effective numbers of electrons were calculated according to Eq. (7). Differential capacitance values were calculated from potentiodynamic charging curve data obtained by cyclic voltammetry at a potential scan rate of 1 mV/s. The average capacitance was calculated according to Eq. (8):

$$C = \frac{Q}{\Delta E} = \frac{\int Idt}{\Delta E} \tag{8}$$

where ΔE is the potential difference corresponding to two points on the I, t voltammetric curve, and t is the time. Potentiodynamic charging curves were obtained in 0.20 M

Fig. 1 Examples of capacitance curves in the experimental range of potentials: **a** AG-3 activated carbon, **b** cupric ion composites, **c** iodide-doped polypyrrole composites

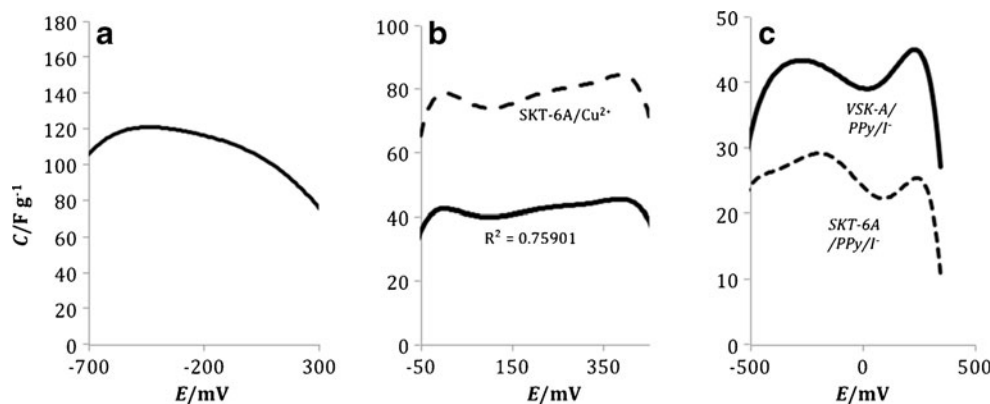


Table 1 Average experimental values of differential capacity and applicable ranges of hemosorbent potential

Hemosorbent	C_a (F g ⁻¹)	Potential range (mV)
AG-3 activated carbon	100	-950 to +450
SKT-6A activated carbon	30	
VSK-A activated carbon	75	
AG-3/Cu ²⁺ composite	40	-50 to +450
SKT-6A/Cu ²⁺ composite	72	
SKT-6A/PPy/Γ composite	25	-600 to +450
VSK-A/PPy/Γ composite	38	

sodium sulfate solution for unmodified carbons and some experiments with cupric ions and in 0.15 M sodium chloride solutions in experiments with free hemoglobin adsorption.

Results and discussion

Hemosorbent capacitance

Since the differential capacitance values and the dependence of capacitance on the electrode potential were of great importance in the computation of effective numbers of electrons transferred in the elementary act of adsorption, data on the dependence of electrode capacitance on potential were obtained experimentally. For this purpose, cyclic voltammograms were obtained for each sample of activated carbon or composite material used in the present work, and capacitance values average based on the anodic and cathodic branches of the voltammogram were computed for each potential. Sample *C*, *E* curves are shown in Fig. 1.

As Fig. 1 shows, the capacitances of the investigated materials vary only slightly in the absence of adsorbate. Thus, in determining the values of the effective number of electrons, it is possible to use average values of capacitance C_a over the experimental range of potential values for each adsorbent material, as shown in Table 1. It should be noted

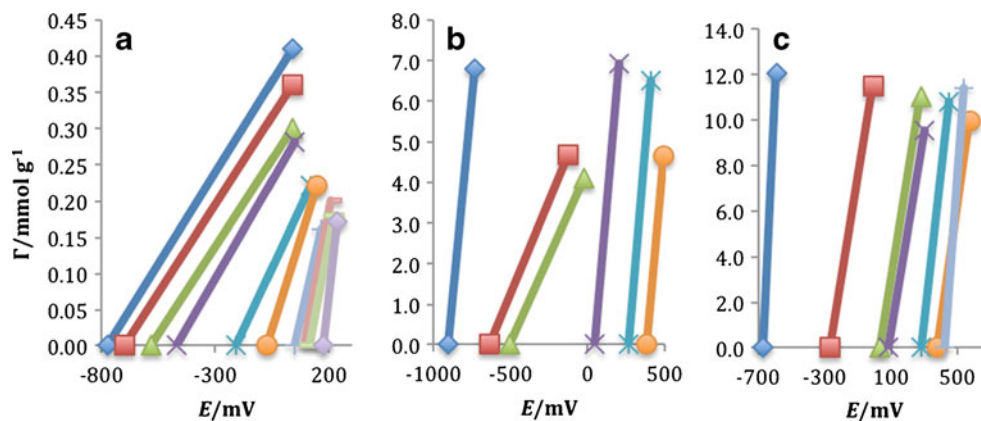
that the values shown in Table 1 are in good agreement with the capacitance values in [14].

Adsorption of model toxicants

Changes in open-circuit potentials of carbon samples ΔE in each experiment were calculated by taking the difference between the open-circuit potentials of the sample before and after the interaction with the toxicant solution. Changes in Gibbs' surface excess $\Delta\Gamma$ for all toxicants were calculated by taking the difference between initial and final concentration of the adsorbed species and dividing by their respective molar masses. Experimental adsorption data for organic (isopropanol and *t*-butanol) and inorganic (cupric ions) toxicants from aqueous solutions on electrochemically modified AG-3 carbon samples with various initial potentials are shown in Fig. 2. From these data, values of the ratio of electrode capacitance to the effective number of electrons C/n and the effective number of electrons n were calculated according to Eqs. (6) and (7). Figures 3, 4, and 5 show the dependences of C/n on initial carbon potential for the three adsorbates, while Fig. 6 shows the calculated values of effective numbers of electrons n for various initial potentials of the AG-3 carbon. The results of isopropanol, *t*-butanol, and cupric ion adsorption experiments are summarized in Tables 2, 3, and 4, respectively.

From the adsorption data for both alcohols, it is obvious that the values of effective numbers of electrons transferred during adsorption of these organic toxicants on AG-3 activated carbon are quite small (0.024 to 0.122). In contrast to this, the values of effective numbers of electrons for cupric ion adsorption (Fig. 6) vary greatly in the experimental range of potentials, with two characteristic areas: Between the open-circuit potential values of -775 to -470 mV, the value of n is near 2, while for potentials more positive than -470 mV, a gradual decrease in the effective number of electrons is observed toward near-zero values, culminating in a slightly

Fig. 2 Gibbs' surface excess (adsorption) as a function of potential during adsorption on AG-3 activated carbon with various initial potentials: **a** cupric ions (CuSO₄), **b** isopropanol, **c** *t*-butanol



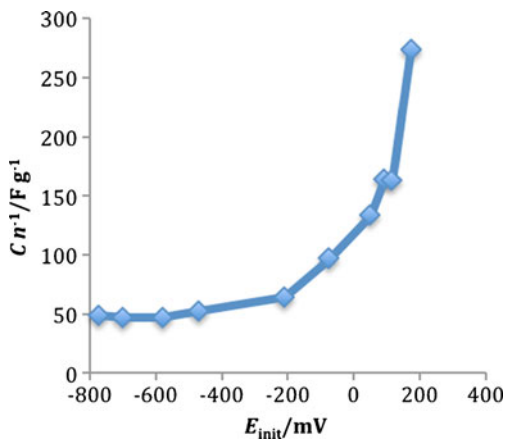


Fig. 3 The rate of adsorption of cupric ions as a function of initial potential of AG-3 activated carbon

negative value $n = -0.040$ for the initial carbon potential $E_i = +475$ mV. This indicates that the carbon sorbent was actually reduced (since $\Delta E = -5$ mV, indicating that electrons were transferred to the electrode from the adsorbate), which could be attributed to a minute amount of cuprous ions in the CuSO_4 solution that become oxidized to cupric ions.

The above results can be considered strong evidence of an adsorption mechanism for the alcohols that does not involve any significant integer-electron charge transfer. This is quite important for the potential use of AG-3 carbon as a hemosorbent, since integer values of effective numbers of electrons may point to the occurrence of faradaic processes accompanied by the formation of new toxic substances in the vicinity of the electrode. Such faradaic processes must be avoided in the process of hemoperfusion [4]. It should be noted that the presence or absence of integer-electron charge transfer is most important in the hemocompatible range of potentials of the hemosorbent itself, which is between -150

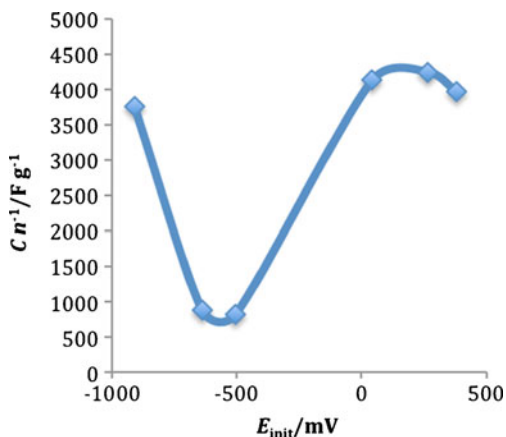


Fig. 4 The rate of adsorption of isopropanol as a function of initial potential of AG-3 activated carbon

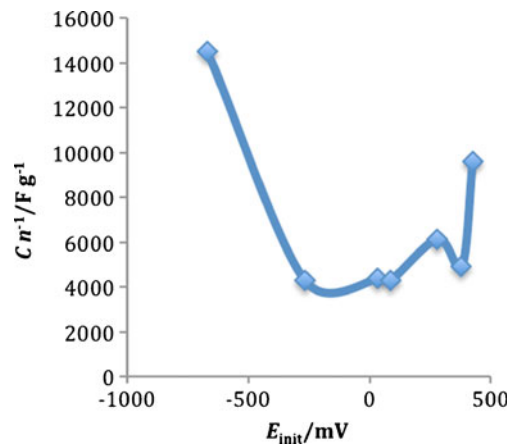


Fig. 5 The rate of adsorption of *t*-butanol as a function of initial potential of AG-3 activated carbon

and $+50$ mV; outside this range, adsorption of blood components with integer effective numbers of transferred electron occurs regardless of the type of adsorption mechanism of the adsorbate [2]. Thus, it would be possible to remove both alcohols from blood by the hemoperfusion method using an electrochemically modified AG-3 activated carbon as the hemosorbent.

On the other hand, cupric ions show strong evidence of a predominantly “faradaic” adsorption mechanism with charge transfer, resulting in the deposition of metallic copper on the surface of the carbon hemosorbent in the range between -775 and -470 mV, since the effective numbers of electrons in this range have values near $n \approx 2$. This process can be described by Eq. (9):



Even for initial potentials of AG-3 activated carbon more positive than -470 mV, where $n \leq 1$, there must be a

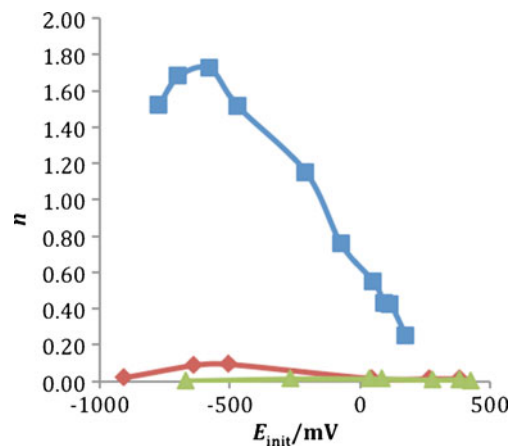


Fig. 6 Effective numbers of electrons as a function of initial potential of AG-3 activated carbon for adsorption of cupric ions (square), isopropanol (diamond), and *t*-butanol (triangle)

Table 2 Characteristics of isopropanol adsorption on AG-3 activated carbon

E_{init} (mV)	ΔE (mV)	$\Delta\Gamma$ (mmol g ⁻¹)	n
-910	+175	6.95	0.027
-640	+513	4.52	0.114
-505	+483	6.69	0.122
+43	+162	4.95	0.024
+265	+148	4.00	0.024
+382	+113	6.56	0.025

significant contribution of the two-electron adsorption mechanism, although some copper must also be adsorbed as cupric ions (without any charge transfer). The appearance of a characteristic reddish-pink color on the adsorbent surface can serve as further evidence of the two-electron mechanism described by Eq. (9), which is similar to the process of electroless contact deposition [15] (it should be noted that while instances of noble metal deposition on carbon materials have been described [16], to date there is no indication in literature as to the relationship between this phenomenon and the open-circuit potential of the carbon material). Finally, for potentials above +475 mV, it is likely that the predominant mechanism of adsorption would be that of Cu²⁺ ions without any appreciable charge transfer (with numbers of electrons near zero), which is also confirmed by the absence of the characteristic reddish-pink deposit on the sorbent granules.

If it is supposed that the only mechanisms of Cu²⁺ adsorption on the AG-3 carbon are the two-electron charge transfer adsorption shown in Eq. (9) and the adsorption of cupric ions without charge transfer, the computed values of effective numbers of electrons should reflect the ratio between the two processes for any given hemosorbent potential. For the predominantly two-electron process potential range, it can be assumed that all of the copper is adsorbed by this mechanism, while in the “transition” range more

Table 3 Characteristics of *t*-butanol adsorption on AG-3 activated carbon

E_{init} (mV)	ΔE (mV)	$\Delta\Gamma$ (mmol g ⁻¹)	n
-670	+80	5.95	0.014
-267	+259	6.47	0.043
0	+165	5.38	0.027
+35	+245	4.86	0.046
+85	+215	5.01	0.046
+280	+170	6.04	0.035
+380	+195	6.56	0.034
+425	+115	5.97	0.018

Table 4 Characteristics of cupric ion adsorption on AG-3 activated carbon

E_{init} (mV)	ΔE (mV)	$\Delta\Gamma$ (mmol g ⁻¹)	n
-775	+815	0.319	2.07
-700	+740	0.361	2.13
-580	+620	0.300	2.15
-470	+517	0.280	1.91
-210	+330	0.220	1.55
-75	+220	0.199	1.04
+50	+116	0.159	0.755
+92	+118	0.195	0.626
+115	+107	0.179	0.619
+175	+60	0.169	0.367
+475	-5	0.130	-0.040

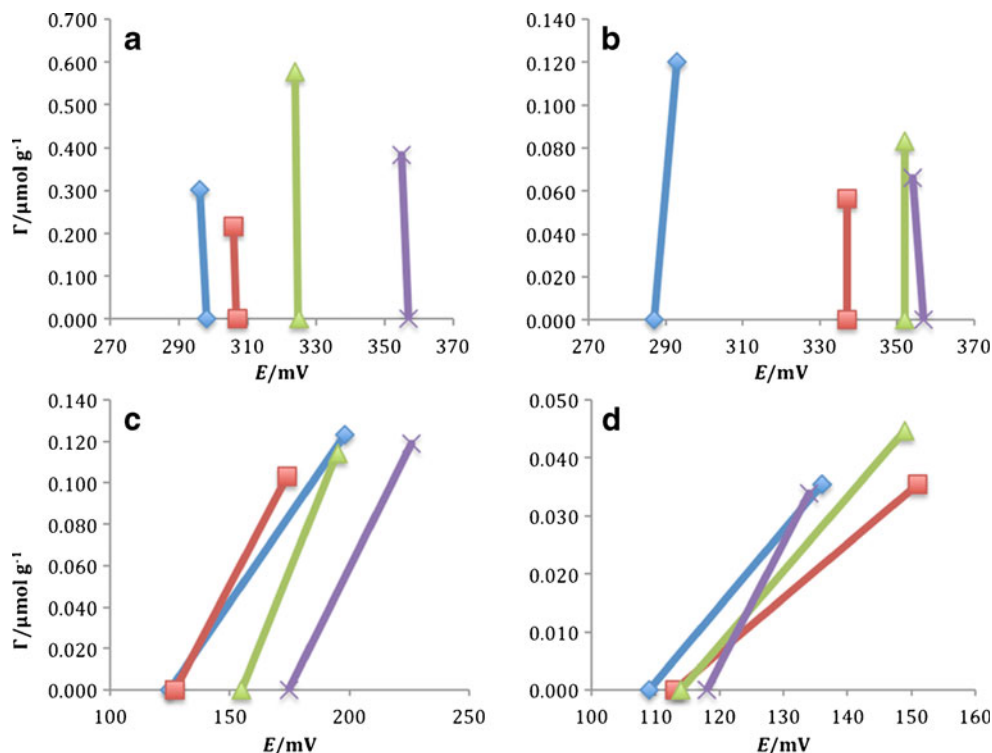
positive than $E=-470$ mV, the contribution of the mechanisms with and without charge transfer can be calculated simply as the ratio of the value of effective number of electrons for each respective initial carbon potential to $n=2$. The percentage contributions thus calculated from n values are summarized in Table 5. It should be emphasized that, regardless of the relative contribution of either mechanism, shifts in the open-circuit potential of the AG-3 activated carbon occurred in each of the experiments, which serves as evidence of the electrochemical nature of both mechanisms of Cu²⁺ interaction with activated carbon hemosorbents.

For practical purposes of hemoperfusion, however, another conclusion can be reached based on the calculated effective charge transfer results. Since the hemocompatible range of potentials for the hemosorbent (between -150 and +50 mV) falls in the range of n values between 0.76 and 1.5, which corresponds to 38–75 % contribution of the two-electron

Table 5 Relative contribution of adsorption with and without charge transfer for cupric ion adsorption on AG-3 activated carbon hemosorbent with various initial potentials

n	E_{init} (mV)	ΔE (mV)	Percent contribution	
			Transfer (%)	No transfer (%)
2.07	-775	+815	100	–
2.13	-700	+740	100	–
2.15	-580	+620	100	–
1.55	-210	+330	78	23
1.04	-75	+220	52	48
0.63	+92	+118	32	69
0.37	+175	+60	19	82
0.04	+475	-5	2	98

Fig. 7 Gibbs' surface excess (adsorption) as a function of potential during adsorption of hemoglobin on composite materials: **a** SKT-6A/Cu²⁺, **b** AG-3/Cu²⁺, **c** SKT-6A/PPy/I⁻, **d** VSK-A/PPy/I⁻



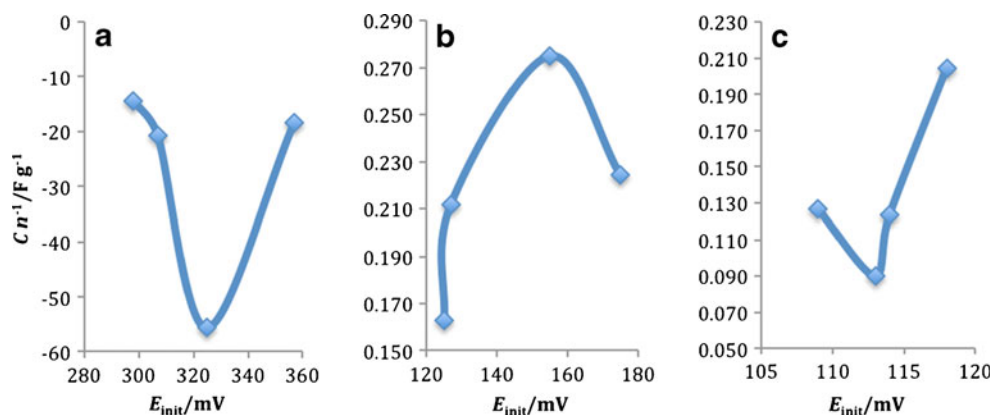
charge-transfer adsorption mechanism and effectively prohibits its use for removal of cupric ions from blood due to the high likelihood of blood protein adsorption on the surface of the carbon, the range of potentials with minimal contribution of the charge-transfer process for copper lies far outside the range of hemocompatibility.

Thus, experimentally determined values of effective numbers of electrons for adsorption processes of toxicants may be used to draw conclusions as to the likely mechanism of interaction and can be used as a criterion of hemosorbent suitability for removal of specific toxicants. The latter suitability check should be performed by calculating effective number of electron values from data obtained within the hemocompatibility range for the carbon.

Adsorption of biological substrates

Since processes of hemo- and plasmosorption are carried out in the presence of various biological macromolecules, it was important to determine the applicability of the effective number of electrons as a source of information about the nature of the processes occurring between the hemosorbent and the biosubstrate. In the present work, free hemoglobin (not constrained within a red blood cell) was used as a biosubstrate. Free hemoglobin has the molar mass of ca. 66 kDa [17], while blood proteins are macromolecular polymers that consist of hundreds or thousands of different amino acid monomers; their molar mass ranges from 6 to 1,000 kDa or

Fig. 8 The rate of adsorption of hemoglobin as a function of initial potential of hemosorbent composite materials: **a** SKT-6A/Cu²⁺, **b** SKT-6A/PPy/I⁻, **c** VSK-A/PPy/I⁻



higher, depending on the number of individual polypeptide chains comprising the protein structure [17].

The importance of investigating the sorption properties of free hemoglobin is due to the considerations of its toxic properties. Free hemoglobin appears in blood plasma as a result of hemolysis (the destruction of red blood cell membranes, e.g., as a result of massive intravascular hemolysis, transfusion of incompatible blood, or other pathological states) and is highly toxic due to the development of tissue hypoxia (decreased oxygen transport to tissue, increased burden on the organism due to the presence of hemoglobin decomposition products, acute tubular necrosis of the kidneys (due to the obstruction and damage of the tubule cells by the large hemoglobin molecules) leading to acute renal failure [18]. Therefore, the problem of free hemoglobin removal from blood and blood plasma is very important, and a solution involving the use of electrochemically controlled hemo- or plasmasorption [2] appears to be quite promising.

Hb adsorption experiments were carried out with three brands of initial activated carbon (AG-3, VSK-A, and SKT-6A), as well as with four activated-carbon composite materials: two with cupric ions (AG-3/Cu²⁺ and SKT-6A/Cu²⁺) and two with iodide-doped polypyrrole (SKT-6A/PPy/I⁻ and VSK-A/PPy/I⁻). The change in Gibbs' adsorption was calculated from the measurements of Hb concentration before and after immersing the hemosorbent in an aqueous model solution of free Hb. The adsorption and initial hemosorbent potential data for all hemosorbents are shown in Fig. 7. The C/n ratio was calculated according to Eq. (6) and depicted in Fig. 8 as a function of potential for SKT-6A/Cu²⁺, SKT-6A/PPy/I⁻, and VSK-A/PPy/I⁻. Finally, the effective number of electrons was calculated according to Eq. (7) for each initial hemosorbent potential and shown in Figs. 9 and 10 as a

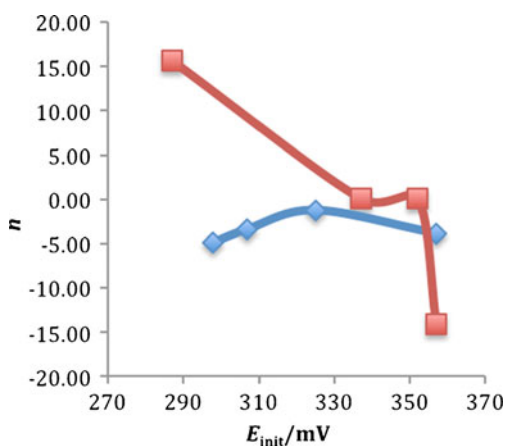


Fig. 9 Effective numbers of electrons for adsorption of hemoglobin as a function of initial potentials of composite hemosorbent materials containing cupric ions: SKT-6A/Cu²⁺ (diamond) and AG-3/Cu²⁺ (square)

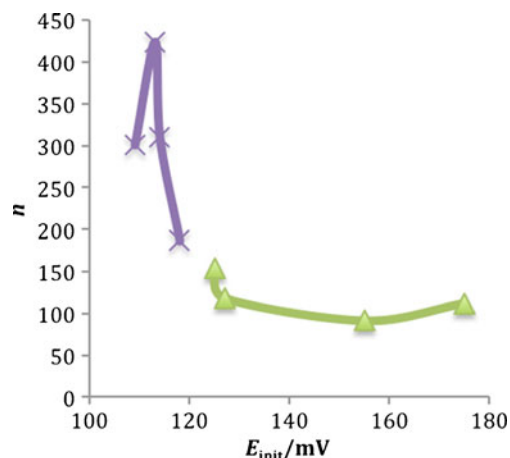


Fig. 10 Effective numbers of electrons for adsorption of hemoglobin as a function of initial potentials of composite hemosorbent materials containing iodide-doped polypyrrole: SKT-6A/PPy/I⁻ (triangle) and VSK-A/PPy/I⁻ (multiplication symbol)

function of the initial hemosorbent potential for the copper and PPy/iodide composites, respectively. A summary of the relevant data and calculated results for the adsorption of Hb is given in Table 6.

At first glance, many of the calculated values for the effective number of electrons transferred in the course of Hb adsorption from aqueous solutions may appear abnormally large. However, other authors [19–21] have also described electrochemical processes involving charge transfer to/from macromolecular biochemical compounds that are characterized by very large effective numbers of electrons (computed by other methods). For instance, electroreduction of albumin at a dropping mercury electrode was observed to require the transfer of 10.5 electrons [19]. A study of the adsorption of proteins on the surface of carbon nanotubes [20] showed that the adsorption of one amino group required 0.04 electrons; considering that the number of amino groups per molecule of protein was 23,000 to 75,000, the authors of [20] computed the total effective number of electrons transferred per molecule of protein which is in the range of 920–3,000 electrons. The study of electrochemical behavior of ferritin, an intracellular protein that stores and releases iron, by cyclic voltammetry [21] has also indicated the involvement of 1,500 electrons in the oxidation/reduction process. Thus, the values of effective numbers of electrons obtained in the present work for the adsorption of free Hb from aqueous solutions agree well with the literature data.

A comparison of the calculated effective numbers of electrons as a function of hemosorbent initial potential with the adsorption dependence on potential for the SKT-6A/Cu²⁺ composite revealed that the potential of maximum adsorption ($E=+325$ mV) corresponds to the minimum absolute value of the effective number of electrons (Fig. 11a). On the contrary,

Table 6 Effective charge transfer for adsorption of free hemoglobin on carbon- and composite-based hemosorbents

Hemosorbent	E (mV)	ΔE (mV)	C (F g ⁻¹)	$\Delta\Gamma \times 10^8$ (mol g ⁻¹)	n
AG-3	105	14	71.9	9.26	1,127
VSK-A	52	10	71.9	10.9	713
SKT-6A	221	11	27.0	36.0	89.2
AG-3/Cu ²⁺	287	6	32.0	12.1	16.4
	357	-3	32.0	6.68	-14.8
	352	0	32.0	8.31	0.0
	337	0	31.8	5.57	0.0
	256	35	54.8	38.1	52.2
SKT-6A/Cu ²⁺	325	-1	84.8	57.7	-1.5
	298	-2	82.3	30.1	-5.7
	357	-2	85.8	38.3	-4.6
	307	-1	81.9	17.2	-4.9
	375	-8	74.5	38.1	-16.2
SKT-6A/PPy/I ⁻	155	40	22.6	11.4	82.1
	175	51	24.8	11.8	111
	125	73	22.8	12.3	140.
	127	47	22.8	10.3	107
VSK-A/PPy/I ⁻	113	38	37.9	3.54	421
	118	16	39.8	3.38	195
	109	27	25.1	3.54	198
	114	35	37.9	4.47	307

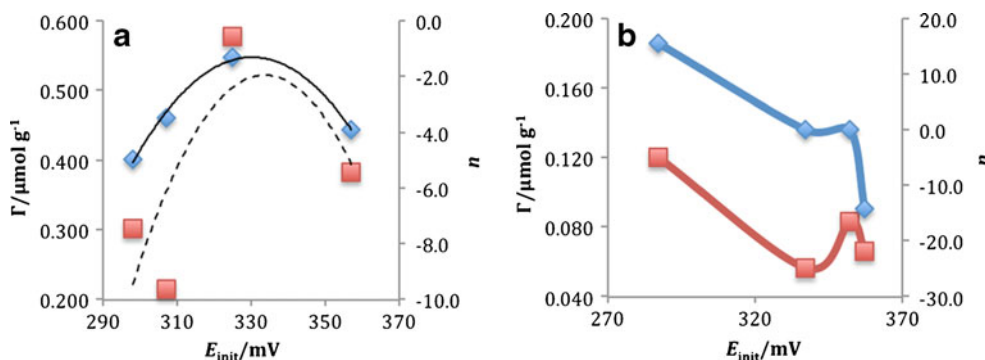
for the AG-3/Cu²⁺ composite, a similar comparison showed the correlation of the maximum adsorption potential with the maximum absolute value of the effective number of electrons (Fig. 11b).

It is also important that, for the AG-3/Cu²⁺ composite, most of the calculated effective numbers of electrons are positive, whereas for the SKT-6A/Cu²⁺ composite they are mostly negative. The observed difference in behavior of the two modified activated-carbon materials is undoubtedly related to the differences in the nature of their interaction with the adsorbate. Obviously, when Hb molecules are adsorbed on the AG-3/Cu²⁺ composite, reduction of the functional groups of Hb must predominate, whereas for the SKT-6A/Cu²⁺ composite, on the contrary, oxidation of the functional

groups of Hb should predominate. For both composites with iodide-doped polypyrrole (SKT-6A/PPy/I⁻ and VSK-A/PPy/I⁻), the effective numbers of electrons were positive, i.e., free Hb adsorption on their surface is accompanied by the reduction of the Hb substrate that is likely aided by the presence of I⁻, a mild reducing agent, in the structure of the composite hemosorbent.

The foregoing analysis serves as a good illustration of the advantages of using calculated values of the effective number of electrons to elucidate the nature of interaction between macromolecular adsorbates and composite hemosorbents. Thus, the study of adsorption of macromolecular biological compounds on activated carbons and carbon-based composite materials (modified with cupric

Fig. 11 Adsorption of free hemoglobin (square) and effective charge transfer (diamond) as a function of initial potential of hemosorbent composite materials: **a** SKT-6A/Cu²⁺, **b** AG-3/Cu²⁺



ions and iodide-doped polypyrrole) has shown that the determination of effective numbers of electrons contributes greatly to the understanding of the mechanism of such adsorption interactions in the same way as observed for adsorption of cupric ions and alcohols.

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