

A Carbon Paste Electrode Modified with Bituminous Coal for Studying Its Sorption Properties

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Abstract: Sorption properties of bituminous coal sample were studied by means of voltammetry on the coal modified carbon paste electrode. Influence of the presence of alkylammonium cation and the temperature on the sorption of metals was studied and interpreted, too. An inhibition effect of hexadecylammonium bromide, as well as of the increasing temperature, was observed for three metals; namely, cadmium, lead, and copper.

Keywords: Carbon paste electrode; Modified carbon paste; Coal; Adsorption of metal ions

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Introduction

Adsorption properties of natural as well as oxidized coals depending on their porous structure, high surface area and the surface functional groups have been extensively studied from the point of their use as the possible adsorbents [1-3]. Immobilization of copper, cadmium, and lead on the altered bituminous coal was supposed to take place by means of cation exchange due to the presence of the carboxylic groups [4]. The adsorption of anionic surfactant sodium dodecylsulphate on various types of coal is probably connected with interactions between hydrophobic chain and coal surface [5]. The surface adsorption mechanism of cation surfactant hexadecyltrimethylammonium bromide on the bituminous coal is based on the hydrophilic interactions, too [6]. Mostly, the adsorption experiments have been performed in the batch mode, which is rather time consuming. Open-circuit voltammetry or multisweep cyclic voltammetry on the modified carbon paste electrodes offers relatively fast and easy method to examine possible sorbent [7].

Traditional carbonaceous materials, mainly spectroscopic carbon / graphite, as well as novel materials (such as carbon nanotubes, nanofibers, or fullerenes) can be used as modifiers of carbon paste electrodes (CPEs) [8]. Probably, the first preparation and characterization of the coal modified CPE was described in the work using sub-bituminous and bituminous coal [9]. The prepared electrodes exhibited the satisfactory potential range in the common aqueous electrolytes and the quasi-reversible electron-transfer kinetics. Open-circuit sorption of Cu^{2+} , Cd^{2+} , and Pb^{2+} proved the adsorption on the coal modifier comparable with that on clay minerals. It was concluded that the coal electrode represents the useful tool for studying the adsorption of metal ions onto the coal material.

By following the former results [9], this work was aimed at the studies on sorption of Cd^{2+} , Pb^{2+} , and Cu^{2+} and the effect of alkylammonium cation and the temperature.

Experimental

Chemicals, Reagents, Stock and Standard Solutions

Bituminous coal sample (C; with particle size of 0.25–0.8 mm) was obtained from Ostrava-Karvina Coal Mines District and used as the electrode modifier of choice. Characteristics of this coal sample are gathered in Table I.

Table I. *Preliminary and ultimate analysis of coals.*

Coal	W^a (%)	A^d (%)	VM (%)	C^{daf} (%)	H^{daf} (%)	N^{daf} (%)	O^{daf} (%)	S_t^d (%)
C	1.7	6.6	35.3	85.6	5.4	1.1	6.5	1.3

W^a – moisture content A^d – ash content (dry basis)

VM – volatile matter content (dry, ash-free basis)

C^{daf} , H^{daf} , N^{daf} , O^{daf} – carbon, hydrogen, nitrogen, oxygen content (dry, ash-free basis)

S_t^d – total sulphur content (dry basis)

Carbon paste electrode [CPE(C); content of modifier: 10 %, w/w] was prepared according to the already described procedure [9]; when the technique of choice for measurements with CPEs being also already described [7,10].

Both main chemicals used – sodium acetate and acetic acid for the preparation of acetate buffer (pH 3.6) were of analytical reagent grade (Merck). Hexadecyltrimethylammonium bromide (HDTM) (Sigma-Aldrich) of analytical reagent grade was used as stock solution made 0.001 mol.l⁻¹ in concentration. Stock standard solutions of Pb²⁺ (4.83 × 10⁻³ M), Cd²⁺ (8.9 × 10⁻³ M), and Cu²⁺ (1.57 × 10⁻² M) were prepared from Titrisol standard (Merck). Redistilled water (glass apparatus) was used throughout the experiments; the glassware was cleaned as described [10].

Electrochemical Apparatus and Procedures

EKO-TRIBO-Polarograph (EKOTREND, Prague, CZ) was employed for all the voltammetric measurements. A three-electrode cell was equipped with a carbon paste electrode (CPE) (working), an Ag/AgCl (sat. KCl) reference electrode and a Pt-wire counter electrode. Differential pulse voltammetry (DPV) was carried out at a scan rate of 20 mV s⁻¹ with a pulse amplitude of 50 mV and a pulse width of 100 ms, within the potential range from -1.0 V to +0.2 V vs. ref.

Open-circuit sorption was performed by soaking of CPE(C) in the solution of metals for a selected time (without applied potential). Thereafter the electrode was removed, carefully wiped and immersed into the background electrolyte. To detect the adsorbed metals, anodic stripping voltammetry in the differential pulse mode was employed under the conditions stated above.

Results and Discussion

Open-Circuit Sorption of Selected Metal Ions

A sorption ability of various samples of coal was already tested by means of the coal modified carbon paste electrode [9]. Among the samples tested (brown coal and bituminous coal) the highest sorption was found to occur on the bituminous coal used also in this work. Open-circuit sorption (*i.e.*, without potential applied) of Cd²⁺ (4.45 × 10⁻⁵ M), Pb²⁺ (4.83 × 10⁻⁵ M), and Cu²⁺ (1.57 × 10⁻⁵ M) in 1 × 10⁻³ M KCl (simultaneous sorption of all the metals) was performed with the sorption time for 600 s.

After medium exchange DPV in the acetate buffer pH 3.6 was measured. The current enhancement on the modified electrodes in comparison with the unmodified CPE(0) is caused by sorption of the metal ions onto the coal surface even if no deposition potential was used (see Table II overleaf).

Table II. *Differential pulse voltammetric current responses of metal ions adsorbed onto the coal-modified carbon paste electrode, CPE(C). Exp. conditions: $c = 4.45 \times 10^{-5}$ M Cd^{2+} , 4.83×10^{-5} M Pb^{2+} , and 1.57×10^{-5} M Cu^{2+} ; Sorption solution in 0.001 M KCl; sorption time: 600 s; DPV after medium exchange, acetate buffer (pH 3.6).*

Electrode	I_{cd} (nA)	I_{pb} (nA)	I_{Cu} (nA)
CPE(0)	0	0	0
CPE(C)	146	212	57

The metals adsorption on coal probably goes due to interactions with suitable function groups on the coal surface [2]. In comparison with other sorbents such as clay minerals exhibiting ion exchange into interlayer of structure [11], one could expect a lower sorption in the case of coal. However, our results did not fully proved this presupposition as the obtained current responses on CPE(C) are comparable with those on the montmorillonite modified CPEs {50 – 300 nA (Cd^{2+}), 50 – 100 nA (Pb^{2+}), and 20 – 100 nA (Cu^{2+})} depending on the type of montmorillonite [12]. It can be concluded that, among the metals studied, the coal sample chosen has exhibited the highest sorption ability for Pb.

Effect of Hexadecyltrimethylammonium Cation

A negative effect of presence of alkylammonium cations on the metals sorption on various sorbents was already described in the case of clay minerals [13,14] as well as coal [6]. The significant decrease of copper sorption was found both in the presence of HDTM in the sorption solution and on the adsorbent pre-treated with HDTM. For example, the adsorption ability of Cu^{2+} was decreased to 57 % on the coal primarily modified with HDTM in comparison with the original bituminous coal sample [6]. Supposing a formation of π -complexes between the hydrophilic end of HDTM and the aromatic components of coal, only a part of the coal surface area is available to the Cu^{2+} sorption.

The HDTM presence in the sorption solution can be illustrated by the following results obtained for cadmium and lead. The HDTM concentration was comparable with those of the metals (at a concentration of 1×10^{-5} mol.l⁻¹).

The negative effect of the presence of HDTM is more significant than for the coal sample modified with HDTM. The sorption was decreased to 18 % (for Cd^{2+}) and 20 % (Pb^{2+}). Here, it can be stated that the same results have been obtained by means of voltammetric measurements in combination with CPEs modified with a montmorillonite clay (see [14]).

And similarly, almost identical dependences on the HDTM presence could also be obtained by the sorption studies performed by batch mode on montmorillonites and their derivatives containing various alkylammonium cations or on montmorillonites in the presence of alkylammonium cations in the sorption solutions [15].

Effect of Temperature

The temperature changes and the resultant effect upon the sorption of metals onto the coal-modified CPE can be studied by means of voltammetry, too. In general, the sorption of metals significantly decreases with the increasing temperature, which is shown in Fig. 1 below – in the case of the sorption of Cd^{2+} ions at various temperatures of the solution selected to study the respective sorption process.

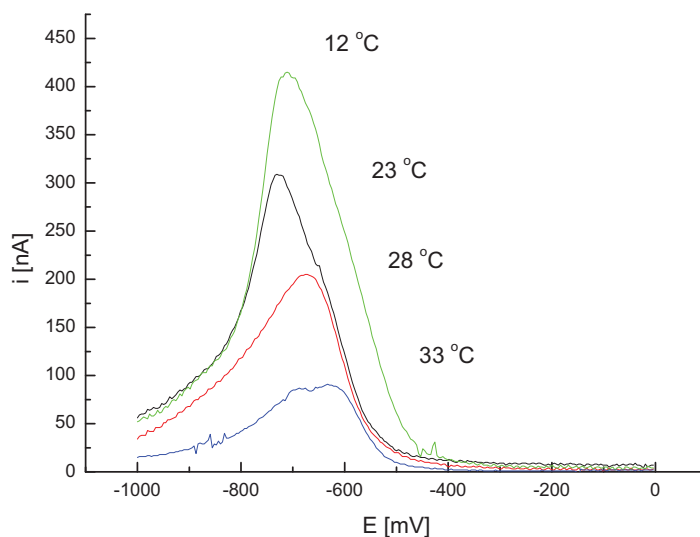


Fig. 1: DPV of Cd^{2+} sorbed on CPE(C) at various temperatures.

Exp. conditions: $c = 4.45 \times 10^{-5}$ M Cd^{2+} , DPV after medium exchange, acetate buffer pH 3.6.

The temperature of the background electrolyte after medium exchange — i.e., acetate buffer (pH 3.6) — was kept in the temperature range of 23–25 °C. The same dependences were found in the case of Pb^{2+} .

The sorption increase at the lower temperatures exhibited the positive effect in the presence of HDTM. In contrast with the results given in Table III, the decrease of the sorption of Cd^{2+} is not so significant and the sorption intensity has decreased only to 45 % under the condition of a temperature of 5 °C (see Table IV).

Table III. *Differential pulse voltammetric (DPV) current responses of Cd^{2+} and Pb^{2+} adsorbed onto CPE(C).* Exp. conditions: $c = 4.45 \times 10^{-5}$ M Cd^{2+} and 4.83×10^{-5} M Pb^{2+} ; sorption time: 600 s; DPV after medium exchange, acetate buffer (pH 3.6)

Sorption solution	I_{Cd} (nA)	I_{Pb} (nA)
Cd^{2+} and Pb^{2+}	261	316
+ 10^{-5} M HDTM	47	63

Table IV. *Differential pulse voltammetric (DPV) current responses of Cd^{2+} adsorbed onto CPE(C) at various temperatures.* Experimental conditions: $c = 4.45 \times 10^{-5}$ M Cd^{2+} ; sorption time: 600 s; DPV after medium exchange, acetate buffer (pH 3.6)

Sorption solution	I (nA) at 23 °C	I (nA) at 5 °C
Cd^{2+} (alone)	261	375
+ 10^{-5} M HDTM	47	167

Conclusions

The carbon paste electrode modified with bituminous coal, CPE(C), has shown to be suitable to study the adsorption of cadmium, lead, and copper ions onto the bituminous coal. The most intensive sorption onto the sample of coal tested was observed in the case of Pb^{2+} , whereas Cu^{2+} exhibited the lowest adsorption capability.

A significant effect of inhibition in the presence of HDTM was achieved at the ambient laboratory temperature, when the inhibition could be eliminated by the decrease of temperature under $t = 10$ °C. Generally, the sorption of Cd^{2+} and Pb^{2+} decreased with the increasing temperature and the sorption was not measurable above the temperature of 35 °C.

The advantages of measurements with the coal-modified CPE can be seen mainly in a relatively fast testing of various parameters that may influence the adsorption process (e.g.: pH, the presence of ligands, varied temperature) compared to a related experimentation in the batch mode [6,15].

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