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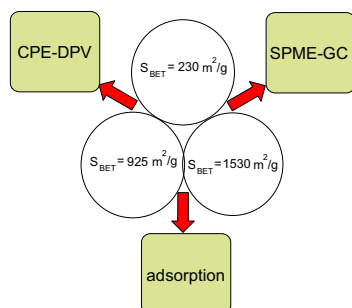
The adsorptive properties of powdered carbon materials with a strongly differentiated porosity and their applications in electroanalysis and solid phase microextraction



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GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption of 4-chlorophenol from an aqueous solution on carbonaceous materials (one carbon black and two powdered activated carbons) with a strongly differentiated porosity was investigated. The kinetic data were fitted well to the pseudo-second order model. The amount of 4-chlorophenol adsorbed at equilibrium was increased with an increase in the specific surface area of the tested materials. The adsorption isotherms were analyzed using the Langmuir and Freundlich models. The Langmuir isotherm was slightly favorable ($R^2 > 0.99$) rather than the Freundlich isotherm ($R^2 > 0.98$). Carbon materials were also used for the modification of carbon paste electrodes as well as for the preparation of novel solid phase microextraction fibers. The peak current of the differential pulse voltammetry curves was increased along with the amount of added carbon paste electrode modifier. The signal response was closely related to the porosity of the materials used, and increased with the increase in the specific surface area. The amount of 4-chlorophenol extracted from the samples by the solid phase microextraction fiber's surface was also correlated with the specific surface area of the tested materials. All the novel fibers were better than the commercially available fibers prepared from polydimethylsiloxane.

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1. Introduction

Chlorophenols are some of the most important contaminants existing in the environment produced as by-products in many

industrial processes [1]. They are present in drinking water as a result of the chlorination of phenols during disinfection, as biocides, or as degradation products of chlorinated pesticides [2]. Chlorophenols cause an unpleasant taste and odor of drinking water and can exert negative effects on different biological processes [2]. It is well known that chlorophenols are toxic at low levels and persistent in the environment [3,4]. Thus, it is

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important to prevent their release into the environment. Due to their toxicity and persistence, the water monitoring for the presence of chlorophenols as well as their degradation and removal from water are extremely important. Several methods are used to remove chlorinated phenols from water, including biodegradation [3,5], photodegradation [6], advanced oxidation processes (AOPs) [7,8] and adsorption [9–17]. Amongst the numerous methods of chlorophenols removal, adsorption is the procedure of choice and gives the best results. The major advantages of an adsorption treatment for the water purification are less investment in terms of initial development cost, easy operation, and no generation of toxic substances.

The work investigated the properties of three carbon materials with substantially different porosities, as well as their effectiveness as adsorbents for the removal of 4-chlorophenol from aqueous solutions. The one carbon black and two powdered activated carbons were chosen as adsorbents. The criterion for the choice of such materials was the considerable difference in the specific surface area (at least six hundred m^2/g). Water treatment requires adequate analysis and monitoring which includes the determination of contaminants at low concentrations. Therefore, the usefulness of these carbon materials in electroanalysis and solid phase microextraction (SPME) was investigated.

Solid phase microextraction (SPME) was developed as a solvent-free sample preparation technique by Arthur and Pawliszyn [18]. Pawliszyn et al. [19,20] first applied SPME in the analysis of chlorophenols in water samples. The extraction yield of chlorophenols is significantly dependent on the sample matrix [20]. Lee et al. [21] have set the optimal conditions for the determination of the landfill leachate of chlorophenols. The compounds were analyzed by GC–MS. Studies have shown that the matrix not only inhibits the diffusion of the chlorophenols to the SPME fiber coating, but also inhibits their absorption onto the fibers. Although they have concluded that an appropriate extension of the extraction time eliminates these problems, it greatly lengthens the time of analysis. The application of the headspace SPME avoids the effect of the impact matrix [22]. The studies of the examined number of the SPME fiber [23] showed that the best results were obtained when the semi-polar or polar fibers were used.

Carbon paste electrodes (CPEs) for many years enjoyed great popularity, mainly due to their low cost and the fact that carbon pastes are easy to prepare and modify [24,25]. Although the modification of carbon paste electrodes has been known for many years [24,25], carbon modifiers such as activated carbon or carbon black have been used only in a few works for the determination of catechol [26] and metformin [27].

In this study, we evaluated a new SPME fiber coated with three different carbon materials and their efficiencies for the extraction of 4-chlorophenol from aqueous solutions. Selected materials were also examined as modifiers of the carbon paste electrodes (CPEs).

2. Experimental

2.1. Materials

The 4-chlorophenol (4-CP) and trifluoroacetic acid (TFA) were from Sigma (St Louis, USA). The methylhydrosiloxane [(50–55% methylhydrosiloxane)–dimethylsiloxane–copolymer] (MHS–DMS) and methyltrimethoxysilane (MTMOS) were purchased from ABCR GmbH & Co. KG (Karlsruhe, Germany). The pure sodium hydroxide (NaOH), hydrochloric acid (HCl) and sodium sulfate (Na_2SO_4) were obtained from Chempur (Piekary Slaskie, Poland).

The Vulcan XC 72 carbon black (CB) (Cabot Corporation, USA), L2S powdered activated carbon (AC1) (Ceca, France) and modified granular activated carbon R3ex (AC2) (Norit, The Netherlands) [28]

were chosen as adsorbents. The commercial Norit R3ex carbon was demineralized with concentrated HF and HCl acids [28]. A suitable powdered sample (33% initial mass of the granule) was obtained by a method in which the other layer of the granules were abraded in a spouted bed [28,29].

Prior to use, the carbonaceous materials were dried in an oven at 130 °C to a constant mass and stored in a desiccator. The materials to be tested were characterized texturally by means of N_2 adsorption–desorption isotherms at 77.4 K (Micromeritics ASAP 2010, Norcross, USA).

2.2. Adsorption

The samples for the kinetic batch measurements were prepared by contacting 40 mg of CB, 20 mg of AC1 or 10 mg of AC2 activated carbon with 40 mL of the 4-CP aqueous solution at a concentration 0.5 mmol/L in an Erlenmeyer flask. The experiments were conducted at 25 °C and an agitation speed of 200 rpm. The amount of sorption at the time t , q_t (mmol/g), was calculated by the Eq. (1):

$$q_t = V \frac{C_0 - C_t}{m} \quad (1)$$

where C_0 and C_t are the initial and the concentration of 4-chlorophenol at the time t (mmol/L), V is the volume of the solution (L) and m is the mass of the adsorbent (g).

For the determination of the adsorption isotherms, 40 mg of CB, 20 mg of AC1 or 10 mg of AC2, and 40 mL of the solutions containing a known concentration of 4-CP (from 0.2 to 2.0 mmol/L) were placed in an Erlenmeyer flask and shaken at 25 °C for 6 h. The uptake of the adsorbate at the equilibrium, q_e (mmol/g), was calculated from the Eq. (2):

$$q_e = V \frac{C_0 - C_e}{m} \quad (2)$$

where C_e is the equilibrium concentration of the adsorbate (mmol/L) in the solution.

The concentrations of 4-chlorophenol in the solutions before and after the adsorption were determined using a UV–Vis spectrophotometer (Cary 3E, Varian, USA) at 274 nm.

All the experiments were carried out in duplicate and the average values were used for further calculations.

2.3. Voltammetry

The differential pulse voltammetric (DPV) measurements were carried out using the potentiostat/galvanostat AUTOLAB (from Eco Chemie B.V., Netherlands), PGSTAT model 20 driven by GPES software, version 4.9. A conventional three-electrode system, consisting of a carbon paste electrode (unmodified or modified) as the working electrode, a saturated calomel reference electrode (SCE) and a Pt wire as the counter electrode, was employed. The unmodified carbon paste electrode was prepared by a hand mixing graphite powder with an appropriate amount of paraffin oil (Nujol) in an agate mortar. The modified carbon pastes were prepared by adding an appropriate amount (2% or 6% m/m) of the carbon modifiers (carbon black or activated carbon) to the graphite powder. Then the unmodified or modified resulting carbon paste was pressed into the end cavity (3 mm in diameter) of the teflon working electrode holder, and the surface was polished on smooth paper. Before the DPV measurements, the influence of the accumulation time on the peak current was determined. All the voltammograms were recorded at a constant temperature of 25 °C.

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