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Application of carbonized hemp fibers as a new solid-phase extraction sorbent for analysis of pesticides in water samples

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HIGHLIGHTS

- Production of cheep pesticides sorbents using the waste hemp fibers as row material.
- Production parameters affect the materials morphology and sorption properties.
- Carbonized and activated carbons from hemp fibers were successfully used for pesticide preconcentration.
- Efficiency of activated hemp fibers comparable with commercial cartridges.

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ABSTRACT

There is a growing interest in utilization of abundantly available materials, bio-mass or industrial byproducts, as precursors for the preparation of carbon materials. Short hemp fibers, acquired as waste from textile production, were used as low-cost precursor for production of carbon materials as a sorbent in the solid-phase extraction, for pesticide analysis in water samples. Different carbon materials were prepared by carbonization of unmodified and chemically modified hemp fibers. Activation of carbonized materials with potassium hydroxide improves sorption properties of carbonized hemp fibers by increasing the specific surface area (up to 2192 m^2/g) and the amount of surface oxygen groups. The following parameters that may affect the solid-phase extraction procedure efficiency were optimized: different elution solvents and the pH value of pesticide solution. Extracts were analyzed by liquid chromatography–tandem mass spectrometry technique. For this study pesticides belonging to the different chemical classes were chosen. Obtained results indicate that carbonized and activated hemp fibers could be successfully applied as a solid-phase sorbent for the pesticide analysis in water samples.

1. Introduction

Activated carbons with high surface area and pore volumes can be prepared from variety of carbonaceous materials such as coal, coconut shell, wood, agricultural or industrial wastes. In the recent years, there is a growing interest in utilization of the low-cost and abundantly available waste materials as precursors for the preparation of carbon materials [1]. The usage of the waste materials represents a special way of recycling and producing useful products. At the same time the cost of waste disposal are minimized. The possibility of using different type of biomass has already been tested for production of the carbon materials [1–11]. Among other biomass types, Reed and Williams [12] have used hemp fibers for obtaining activated carbon. Hemp fibers are lignocellulosic materials, traditionally used for textile production. In our previous work we have show that, due to their specific structure and presence of the surface functional groups, hemp fibers have good sorption characteristic, especially toward heavy metals [13,14]. For that investigation we have used short hemp fibers that represent a waste in textile industry.

The possibility of producing carbon materials with high specific surface areas, microporous structure, high adsorption capacity and degree of surface reactivity brings the variety of application for these materials. Different carbon materials have been widely used as sorbents in the solid phase extraction (SPE) which is an efficient and economical sample preparation technique for preconcentration of the target analyt. This method has been previously applied to the determination of many pesticides in natural water and crops

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due to its substantial advantages such as providing higher concentration factors, decreasing sample preparation time, reducing costs, and requiring less solvent [15–17].

In this work, short hemp fibers obtained as a waste from textile industry was used for production of carbon material samples with different surface characteristics. Surface characteristics of carbon material depend on both carbon precursor nature and parameters of production [1]. For that reason, different carbon materials were obtained by chemical modification of origin short hemp fiber followed by carbonization and activation. Carbonized and activated hemp fibers obtained in this way were used as a sorbent in the solid-phase extraction for pesticide analysis in water samples. The following parameters that may affect the solid-phase extraction procedure efficiency were optimized: different solvents used for pesticide elution from carbonized and activated hemp fibers surface and the pH value of the pesticide aqueous solution. Extracts, obtained after SPE procedure, were analyzed by liquid chromatography–tandem mass spectrometry technique. For this study pesticides belonging to the different chemical classes as triazine (atrazine, simazine, propazine), neonicotinoid (imidocloprid, acetamiprid, thiamethoxam), carbamate (carbofuran, methomyl), organophosphate (monocrotophos, dimethoate, malathion, acephate), hydroxyanilide (fenhexamid), diacylhydrazine (tebufenozide) and phenylurea (linuron) were chosen. The ability of using carbonized and activated short hemp fibers as a sorbent in SPE procedure was comparatively evaluated with two commercial cartridges.

2. Experimental

2.1. Material

Fibers used in this investigation as a starting material for carbonization, were short hemp fibers obtained from ITES Odzaci, Serbia. Short hemp fibers were used as received. For easier manipulation short hemp fibers were cut to the length of few centimeters. Chemical composition of used fibers is: 1.50% water solubles, 0.69% fats and waxes, 1.39% pectins, 78.15% cellulose, 6.06% lignin, 10.72% hemicelluloses.

2.2. Preparation of carbon materials samples

The amount of hemp fibers structural components, especially lignin, hemicelluloses and cellulose, may affect surface characteristics of carbonized materials [18]. In order to obtain a row material with different characteristics, short hemp fibers were chemically modified as it is described in the literature [13]. The progressive removal of the hemicelluloses was brought by treating the fibers with 17.5% NaOH solution, while the lignin was progressively removed by treating hemp fibers with 0.7% $NaClO_2$. The samples obtained by chemical modification along with the original (as received) short hemp fiber were then carbonized at 1000 °C under constant nitrogen flow (150 cm^3/min), with the heating rate of 5 °C/min. The isothermal time at maximum carbonization temperature was 30 min. After carbonization, five samples denoted Ch1, ChL5, ChL60, ChH5 and ChH45 (as it is shown in Fig. 1), were obtained. Further, carbonized unmodified short hemp fibers (Ch1) were chemically activated using KOH as an activating agent in the 2-step process [5]. Carbonized fibers were mixed with KOH pallets in two different KOH:Ch1 weight ratio (1:1 and 2:1). Activation process was carried out in an electrical furnace under the constant nitrogen flow (150 cm^3/min) with the heating rate of 5 °C/min up to the 900 °C. Final temperature was maintained for 30 min. The resulting products after activation were thoroughly washed with tap water and finally distilled water to remove the residual KOH until the pH value of the eluted water ranged from 6 to 7. In this way, two activated carbon samples (denoted ACh1 and ACh2) were obtained. The scheme of production and denotement of all samples are shown in Fig. 1.

2.3. Surface characteristics

2.3.1. Scanning electron microscopy

Surface structure and morphology were studied by scanning electron microscopy (SEM JEOL JSM-6610LV).

2.3.2. Porous properties of carbonized and activated short hemp fibers

Adsorption and desorption isotherms of N_2 were measured on carbonized and activated short hemp fibers at −196 °C, using porosimeter Micromeritics ASAP 2020, Surface and Porosity Analyzer (Micromeritics Instrument Corporation, US). The total pore volume (V_{total}), micropore volume (V_{micro}) and mesopore including external surface area (S_{meso}), were obtained from the adsorption data, using the manufacturer's software ASAP 2020 V3.05 H. Pore size distribution was estimated by applying BJH method [19] to the desorption branch of isotherms and mesopore surface and micropore volume were estimated using the high resolution α_s plot method [20]. The surface area corresponding to the micropores (S_{micro}) was obtained from the difference between S_{BET} and S_{meso}.

2.3.3. Surface oxygen groups

Temperature-programmed desorption (TPD) in combination with mass spectrometry was used to investigate the nature and thermal stability of carbonized and activated short hemp fibers surface oxygen groups. The TPD profiles were obtained using a custom-built set-up, consisting of a quartz tube placed inside an electrical furnace. Sample was outgassed in the quartz tube and subjected to TPD at a constant heating rate of 10 °C/min to 900 °C under high vacuum. The amounts of CO and CO_2 released from the carbon sample (0.1 g) were monitored using an Extorr 300 quadrupole mass spectrometer (Extorr Inc., USA).

2.4. Solid phase extraction procedure

2.4.1. Preparation of the SPE cartridges

The 0.2 g of each carbon samples was packed into the empty cartridge. The polypropylene upper and lower frits were placed at each end of the cartridge to hold the sorbent packing in place. Next, the outlet tip of cartridge was connected to a Visiprep™ SPE Vacuum Manifold and the inlet end of it was connected to a PTFE suction tube whose other end was inserted into pesticides sample solution. The possibility of using carbonized and activated short hemp fibers as sorbents in SPE procedure was tested by using a stock solution of fifteen pesticides mixture. Concentration of each pesticide in solution was 1 ng/mL.

2.4.2. Optimization of the SPE procedure

The optimization of the SPE procedure, as a sample preparation method, is an important process to achieve the highest enrichment efficiency and the best recovery. The following parameters that may affect the SPE procedure efficiency were optimized: different elution solvents and the pH values of the pesticide aqueous solution. For the optimization of elution solvent, four different elution solvents were used: methanol, dichloromethane, acetonitrile and methanol–dichloromethane (1:1). For this experiment, 100 mL of deionized water (without pH adjustment) was spiked with the working pesticides standard solution in order to achieve the concentration of 1 ng/mL for each analyte in the solution. Following the standard procedure [15], the SPE cartridges were preconditioned with 5 mL of selected elution solvent followed by 5 mL of deionized water. Spiked water samples were loaded at the flow