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SOLID-PHASE EXTRACTION OF ESTROGEN HORMONES FROM WATER USING MULTI-WALLED CARBON NANOTUBES AS SORBENT

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ABSTRACT
Multi-walled carbon nanotubes were employed as a sorbent for solid-phase extraction of estrogen hormones (estrone, 17β-estradiol, and 17α-ethinylestradiol) from water solution. The solid-phase extraction (SPE) method was optimized by choosing an appropriate mass of the sorbent, volume, and initial pH of hormone water solution, as well as by choosing an appropriate organic solvent for extraction. Based on the obtained hormone recoveries, the following SPE conditions were chosen as optimal: 100 cm^3 of hormone water solution at initial pH adjusted to 10; 20 mg of the sorbent; and methanol-dichloromethane mixture as elution solvent. Recoveries obtained under the optimal conditions ranged from 70.56 % for estrone, to 81.23 % for 17α-ethinylestradiol, with a relative standard deviation from 9.92 to 18.74 %.

INTRODUCTION
Steroid estrogens are a group of endocrine-disrupting compounds (EDCs) which, even present in very low concentration (ng/l) [1], can have different adverse effects on living organisms [2]. The principal way in which these compounds reach the environment is through municipal wastewater [3]. Since these compounds are present in very low concentrations in the environment, their detection requires the development of an efficient isolation and preconcentration technique.

Multi-walled carbon nanotubes have been used so far as sorbents for many environmental pollutants, due to high adsorption capacity, the wide pH range of application, and the possibility of surface chemistry modification [4] This paper aimed to examine the possibility of using multi-walled carbon nanotubes as sorbent for solid-phase extraction (SPE) of estrone (E1), 17β-estradiol (E2), and 17α-ethinylestradiol (EE2) from water solution. To obtain high recovery values of the SPE method, the following parameters were optimized: volume and initial pH of hormone solution, the mass of sorbent, and type of organic solvent for hormone elution.

MATERIALS AND METHODS
Multi-walled carbon nanotubes (MWCNTs) (Sigma-Aldrich, USA), with the specific surface area of 252 m^2/g (S_{meso} = 236 m^2/g, S_{micro} = 16 m^2/g, V_{micro} = 0.0749 cm^3/g) were used as SPE sorbent for extraction of selected hormones [4]. Applied SPE procedure included: conditioning of SPE cartridges (3 cm^3) loaded with MWCNTs, passing the water solution of the hormones (with an appropriate volume and pH values) through the cartridges, drying under vacuum for 10 min, elution of hormones with suitable organic solvent, followed by evaporation to dryness under N_2, and reconstitution with 1 cm^3 of methanol. The SPE process was optimized to obtain the highest recoveries by choosing an appropriate mass of the sorbent (20, 50, 100 mg), volume (25, 50, 100 cm^3) and pH (5-11) of hormone water solution, as well as organic solvent (methanol - MeOH, acetonitrile – ACN, dichloromethane/methanol mixture - DCM/MeOH) for hormones extraction.

RESULTS AND DISCUSSION

The recoveries of the SPE method using a different mass of MWCNTs sorbent: 20, 50, and 100 mg, are summarized in Table 1. Since sorbent mass does not have a significant influence on the extraction efficiency, the lowest mass of material was chosen for the following experiments.

SPE method was also optimized by choosing an appropriate volume of hormone water solution (Table 2).

According to the results shown in Table 2, the highest recoveries for all tested hormones were obtained for the volume of 100 cm^3, and this volume was chosen as optimal.

Results obtained for optimization of organic solvent are presented in Table 3. The highest recoveries for estrone and 17β-estradiol were gained using DCM/MeOH, while the best result for 17α-ethinylestradiol was achieved with methanol. The mixture DCM/MeOH was chosen as the optimal organic solvent for the simultaneous extraction of all hormones.

Table 1. Recoveries (%) of SPE method obtained using different mass of sorbent

Hormone	Sorbent mass (mg)		
	20	50	100
Estrone	63.9	63.0	63.5
17α-ethinylestradiol	69.3	68.9	66.2
17β-estradiol	52.6	51.7	54.2

Table 2. Recoveries (%) of SPE method obtained using different volume of hormone water solution

Hormone	Volume (cm^3)		
	25	50	100
Estrone	32.1	56.1	60.7
17α-ethinylestradiol	40.9	84.2	97.4
17β-estradiol	34.4	64.9	74.7

Table 3. Recoveries (%) of SPE method obtained using different organic solvents

Hormone	Solvent		
	Acetonitrile	Methanol	DCM/ MeOH
Estrone	49.4	30.9	62.6
17α-ethinylestradiol	61.6	79.2	60.3
17β-estradiol	33.9	23.1	57.6

Recoveries of the SPE method, obtained by examining the influence of initial pH values of the hormone solution are given in Table 4. The pH 10 was chosen as optimal, due to the highest recoveries obtained for all hormones.

Table 4. Recoveries (%) of SPE method at different pH of hormone water solution

Hormone	pH						
	5	6	7	8	9	10	11
Estrone	51	63	49	70	49	72	78
17α-ethinylestradiol	56	63	48	68	46	85	79
17β-estradiol	50	62	49	62	46	71	65

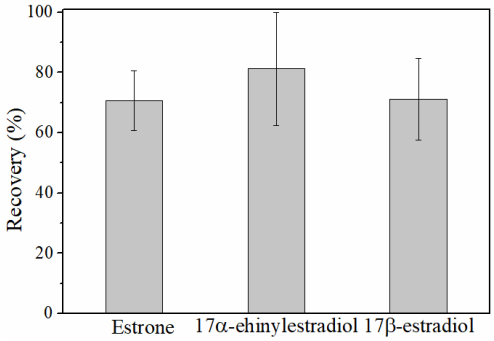

Figure 1. Recoveries of examined hormones obtained using optimized SPE method

The optimum conditions obtained for hormone extraction were the following: 100 cm^3 of water hormone solution with initial pH value adjusted to 10 was passed through the cartridges loaded with 20 mg of MWCNTs, and DCM/MeOH mixture was used as elution solvent.

The optimized SPE method was applied for hormones extraction from water, and obtained recoveries with relative standard deviation are given in Figure 1. Satisfactorily high results were obtained, as recoveries ranged from 70.56 % for estrone, to 81.23 % for 17α-ethinylestradiol, with relative standard deviation from 9.92 to 18.74 %.

CONCLUSION

In this study, MWCNTs were used as sorbents for SPE of estrogen hormones. Parameters of the SPE method were optimized in order to get optimal sorbent mass, volume, and initial pH value of hormone water solution, as well as an optimal organic solvent for elution. Optimized SPE method involves extraction of hormones from 100 cm^3 of water solution, with pH adjusted to 10, using cartridges packed with 20 mg of multi-walled carbon nanotubes, and the mixture of dichloromethane/methanol as elution solvent for hormones extraction. Applying the optimized SPE procedure, high recoveries for estrone, 17β-estradiol and 17α-ethinylestradiol were achieved, which indicates that MWCNTs can be used as an efficient sorbent for hormone extraction from water.

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REFERENCES

[1] M. Auriol, Y. Filali-Meknassi, R.D. Tyagi, C.D. Adams, R.Y. Surampalli, Process Biochem., 2006, **41**, 525–539.
[2] M. Adeel, X. Song, Y. Wang, D. Francis, Y. Yang, Environ. Int., 2017, **99**, 107–119.
[3] H. Hamid, C. Eskicioglu, Water Res., 2012, **46**, 5813–5833.
[4] B. Lalović, T. Đurkić, M. Vukčević, I. Janković-Častvan, A. Kalijadis, Z. Laušević, M. Laušević, Environ. Sci. Pollut. Res., 2017, **24**, 20784–20793.

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