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Evaluation of carbon nanotubes as solid-phase extraction sorbent for the removal of cephalexin from aqueous solution

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ABSTRACT

In this work the ability of carbon nanotubes (CNTs) in adsorption of cephalexin antibiotics at the trace level from aqueous solution has been tested. Samples were strongly adsorbed by CNTs and satisfying recovery was obtained. Analyses of samples were carried out by help of high performance liquid chromatography. To find out the retention capabilities of cephalexin on CNTs, constant amount of each analyte was added to different volumes up to 100 ml and removed by sorbent. Comparing studies between carbon nanotube and silica gel showed higher efficiency of CNTs to silica gel in extracting of cephalexin. The preconcentration of cephalexin on CNTs followed by high performance liquid chromatography allows the detection of 0.15–0.2 μg/ml of cephalosporins. Recoveries of spiked sample analysis in optimum situation ranged from 95.2% to 97.6%.

Keywords: Carbon nanotubes; Solid-phase extraction; High performance liquid chromatography; Cephalexin

1. Introduction

Today all over the world there are lots of pharmaceutical company which produce antibiotics and are causing the water and wastewater be polluted by companies wastes. In this case the risk of antibiotic entrance to the underground water and microorganisms' resistance will occur. To protect the environment and human health efficient facilities of sample preparation and sample preconcentration for accurate analysis seems necessary.

Solid-phase extraction (SPE) is an efficient sample preparation method that is usually used to prepare liquid samples. SPE is suitable for sample extraction, concentration and clean up. They are accessible in wide range of chemistries, adsorbents and sizes. So it has become a common preconcentration method in environmental analytical application recently. Selecting the most suitable product for each application and sample is important. Today different kind of new adsorbent like carbon nanotubes (CNTs) are tested to be used in this extraction packages [1–3,5,11,14].

One group of nanostructures which have been surprisingly in the centre of scientists' attention in recent two decades is carbon nanotubes (CNTs). According to their unique physical and chemical properties, these materials from their discovery time in 1991 by Iijima [11] till now have been used in different fields of application such as development of sensors and biosensors, nanoprobes, drug delivery, nanoelectronic, gas separation, etc. [5,7–9,11,13].

CNTs are considered as hollow graphitic cylinders that have one (single-walled carbon nanotubes, SWCNTs) or more (multi walled carbon nanotubes, MWCNTs) graphene layers. The length of these

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tubes can range from hundreds of nanometers to some micrometers and their diameter for single and multi-wall CNTs comes between 0.2–2 nm and 2–100 nm, respectively [11].

High specific area and hydrophobic surface are two specifications of CNTs that make them capable sorbents for retaining vast amounts of compounds on their surface [6,11]. Extraction of amino acids, proteins, tetracyclins, sulphonamides, phenolic compounds, several phthalate esters, chlorophenols, fungicides, prometryn and cephalosporins are some examples of adsorbed materials by CNTs [1–3,6,10–12,14].

In the present study, the ability of CNTs for determination of cephalosporin in aqueous solution has been examined. The SPE cartridge was self-made in our lab and was packed with MWCNTs. Percentages of remained analytes in the sample were measured by using high performance liquid chromatography and ultra violet (HPLC–UV). At the end, comparing studies between CNTs and silica gel (Si) was performed.

2. Experimental

2.1. Materials

Cephalexin was the target analyte and was taken from Farabi pharmaceutical company (Isfahan, Iran). Chemical structure of the selected compound was shown in Table 1. Acetonitrile (ACN), methanol (MeOH), HPLC grade where obtained from Merck (Darmstadt, Germany). Five hundred μg μl^{-1} standard stock solution of each sample was prepared in deionized water and standard solutions were made by diluting (500 μg l^{-1}) stock solution. Sodium hydroxide and hydrochloric acid were purchased from Merck (Darmstadt, Germany). TLC–silica gel 60 GF which have particle size of 15 μm (Merck, Darmstadt, Germany) was used as comparing sorbent. MWCNTs with an average external diameter of 5–20 nm and apparent density of 150–350 mg/cm^3 were provided by Plasmachem GmbH (Berlin, Germany).

2.2. Chromatographic conditions

Chromatographic experiments were performed by using Alliance HPLC system (Waters, USA) included 515 HPLC pumps, an in-line connected degasser, a 717 plus automatic sample injector, a column compartment and a UV detector. The analytical column was included a C_{18} column (4 × 250 mm: particle size, 10 μm). Isocratic separations for cephalexin carried out using (pH 6, adjusting by $1.7Na_2H_2O_4 1.4KH_2PO_4$/MeOH (78%:22%). The flow rate for these antibiotics was 1.5 ml min^{-1}. The wavelength used to detect cephalexin was set at 229 nm.

2.3. Solid-phase extraction cartridge

The cartridge was made of a 10 ml glass syringe which was packed with 100 mg of sorbent and sorbent was retained by two porous stainless steel disks and cork as frits. Disk's pores size was 50 μm, so we were forced to use a little cork, not to let CNTs washed out. The schematic of the experimental set-up is given in Fig. 1. MWCNTs were purified by 1 M hydrochloric acid (sonicated about 2 h) and washed with water till the sorbent was neutral [6].

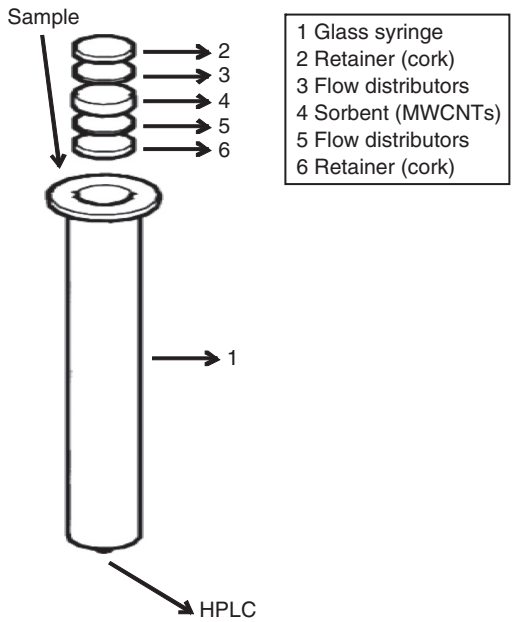
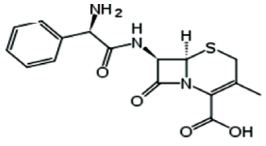


Fig. 1. Schematic of the experimental set-up.

Table 1
Chemical structures of selected compounds [8]

Molecular weight	Chemical formula	Chemical structure	Name
347.39 g/mol	$C_{16}H_{17}N_5O_4S$		Cephalexin

3. Results and discussion

3.1. Desorption conditions

Compounds which have amino group or hydroxyl group were recovered with difficulty and our target analyte belongs to this category [6]. Thus we faced problems for recovery of samples. To catch better recoveries, some tests have been done to optimize the desorption conditions, including composition and volume of eluents.

3.1.1. Composition of eluent

Cephalexin can be eluted by methanol or ACN or the mixture of them. According to Niu and co-workers the best eluent for washing cephalexin from MWCNTs is MeOH/water (9:1) [6].

3.1.2. Eluent volume

To find out the most suitable amounts of eluent in order to get the best recoveries, different volumes of eluent from 2 to 5 ml were examined three times and outcomes are shown in Fig. 2.

3.2. Effect of solution pH

"pH-value plays an important role in the extraction of organic compounds in environmental samples because the pH-value of the sample solution determined the existing state of analytes and the analytes can only be adsorbed in molecule form, so pH of sample solution determined the extraction efficiency of the target analyte" [14]. In this study, the effect of pH was investigated in the range of 2–7. Higher pH was not examined because Cephalexin was instable in alkaline medium [6].

According to the results shown in Fig. 3 pH = 5 is the optimum pH of the sample solution.

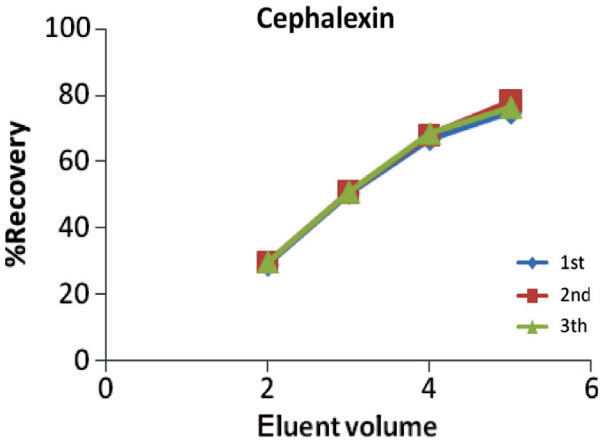


Fig. 2. Effect of eluent`s volume on the recoveries of cephalexin extracted by CNTs. Concentration of analyte, 500 μgL^{-1}.

3.3. Sample volume

To investigate the effect of sample's volume, fixed amount of analyte was solved in different volumes up to 100 ml. After passing the sample over CNTs, CNTs were recovered with optimum eluent volume and sample Ph which were determined in previous steps. As it is shown in Fig. 4 the less the concentration is, the more the recovery is obtained.

3.4. Comparison study

To evaluate the ability of CNTs as a new sorbent for solid-phase extraction cartridge this nanostructure was compared with one common sorbent, named Si. Much more satisfying results were gained for CNTs in comparison to Si. Fig. 5 shows the comparison results obviously.

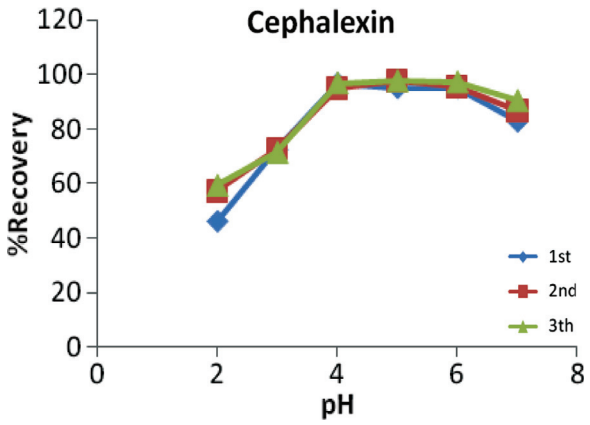


Fig. 3. Effect of pH on the recoveries of cephalexin. Concentration of analyte, 500 µgl–1, eluent volume = 5 ml.

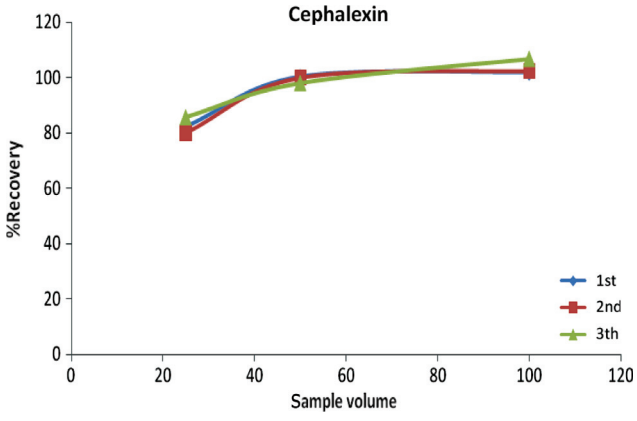


Fig. 4. Effect of sample volume on the recoveries of cephalexin. The analyte amount is fixed and equal to 2.5 µg. Sorbent amount, 100 mg; pH of the solution, pH 5 and eluent volume, 5 ml.

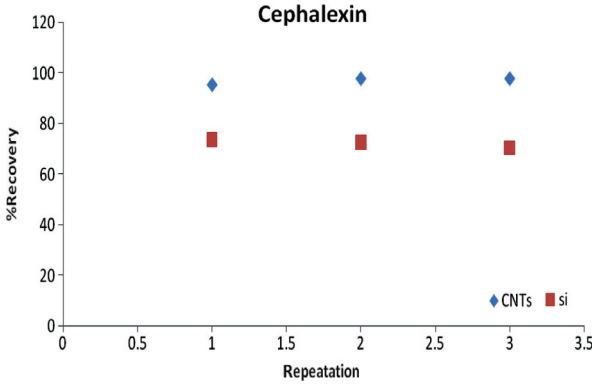


Fig. 5. Comparison between efficiency of CNTs and Si as two different sorbent of solid-phase extraction cartridge. Concentration of each analyte, 500 µg l^{-1}; eluent volume, 5 ml; pH 5.

Table 2
Linear equation, correlation coefficient, detection limit, y = peak area, x = concentration of cephalexin antibiotic

Analyte	Linear equation	Correlation coefficient	Detection limit
Cephalexin	$y = -250.32x + 5.53$	0.9999	0.2 µg/ml

Table 3
Analysis of spiked water samples, RSD (%) (n = 3) = 0.68, recovery (%) average = 96.8

Sample	Added (µg/l)	Found (µg/l)	Recovery (%)
Cephalexin	2.5	2.38	96.1
Cephalexin	2.5	2.40	97.03
Cephalexin	2.5	2.41	97.37

3.5. Analytical performance

Under the optimized conditions, the analytical performance was examined with 10 ml of standard solution. Table 2 shows the analytical features of the proposed method. There is a linear correlation between peak area and concentration.

The method was applied to analysis of tap water samples and was repeated three times and the results are shown in Table 3.

4. Conclusion

In this research, the ability of CNTs as a new sorbent of SPE was tested. Acceptable results proved that these nano materials could be a good alternative for traditional sorbents. Optimum volume for eluent and sample were gained at 5 ml and 100 ml, respectively and maximum amount of recovery was observed in pH = 5. Using small amount of sorbent is the positive point. The results showed that small amounts of eluent are sufficient and when the samples were diluted better recoveries were concluded, so by considering all these results we wish to miniaturize the extraction process by help of CNTs.

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