Determination of cefixime in aqueous solution using multiwalled carbon nanotubes solid- phase extraction cartridge

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ABSTRACT

One of the most important chemical properties of carbon nanotubes is having a hydrophobic surface, and because of that many compounds and materials can be retained on the surface of these nano structures. In this study, by using this feature of carbon nanotubes, their ability in adsorption of cefixime at trace amount from aqueous solution has been tested. Samples were strongly adsorbed by carbon nanotubes and acceptable recoveries were obtained. Analyses of samples were done by high performance liquid chromatography and UV. Limit of detection of cefixime under optimum conditions is ranged between 0.15-0.2痢/ml. recoveries of spiked sample analysis ranged from 86.8% to 88.4%.

Keywords: carbon nanotubes, solid-phase extraction, high performance liquid chromatography, cefixime

1 INTRODUCTION

Today all over the world there are lots of pharmaceutical company which produce antibiotics and are causing the water and waste water be polluted by companies wastes. In this case the risk of antibiotic entrance to the underground water and microorganisms' resistance will occur [1]. 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 are tested to be used in this extraction packages [2-9].

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, nano probes, drug delivery, nano electronic, gas separation and etc [10-14].

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 tubes can range from hundreds of nano meters to some micrometers and their diameter for single and multi wall CNTs comes between 0.2-2 nm and 2-100 nm, respectively [7].

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 [5, 7]. 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 [2-5, 7, 8, 15 and 16].

In the present study, the ability of CNTs for determination of cefixime in aqueous solution has been examined. The solid-phase extraction (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 EXPERINENTAL

2.1 Materials

Cefixime 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). 500 $\mu g \mu l^{-1}$

standard stock solution of each sample was prepared in deionized water and standard solutions were made by diluting (500µgl-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/cm3were provided by Plasmachem GmbH (Berlin, Germany).

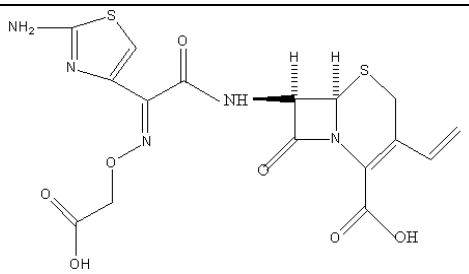
Chemical structure	
Chemical formula	$C_{16}H_{15}N_5O_7S_2$
Chemical weight	g/mol 453/452

Table 1: Chemical structure of cefixime

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 in which wave length used to detect cefixime was set at 254nm . The analytical column was included a C_{18} column (4*125mm: particle size, 5μm) for cefixime. Isocratic separations carried out using (pH 6.5, adjusting by tetra butyl ammonium hydroxide/ACN (3:1)). The flow rate for this antibiotic was 1.5 ml min^{-1}.

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. MWCNTs were purified by 1M hydrochloric acid (sonicated about 2hr) and washed with water till the sorbent was neutral [5].

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

To find out the most capable solvent to wash cefixime from sorbent surface MeOH and CAN were chosen .eluting of cefixime with these eluents was not efficient and satisfactory results were not observed with mixture of MeOH and ACN at studied different ratios. After applying different mixtures of MeOH, ACN, TBAH and water, it was discovered that the most effective solvent for washing cefixime out of CNTs is TBAH/ACN (3:1), so it was accepted as .chosen eluent.

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 5ml were examined three times and outcomes are shown in Fig1.

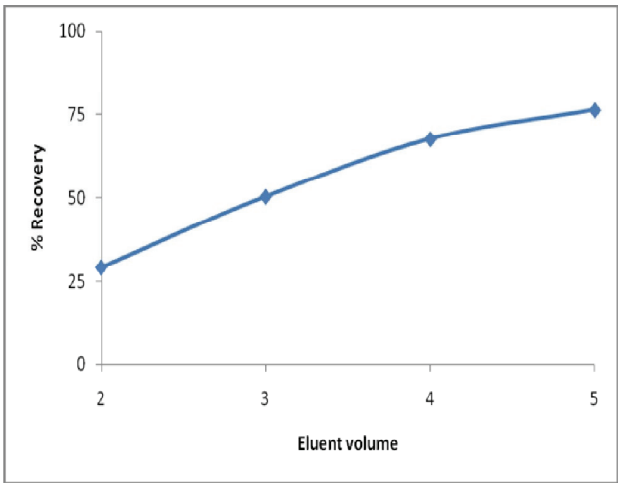


Fig 1: Effect of eluent volume on the % recovery

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 [8]. 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 [5]. According to results shown in Fig 2 pH=5 is the optimum pH of the sample solution.

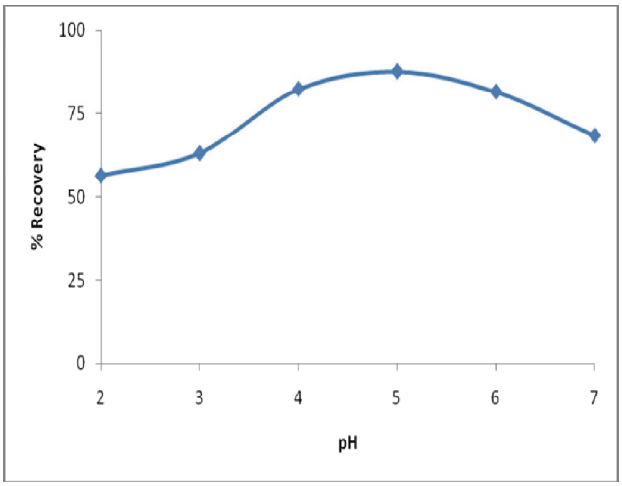


Fig 2: Effect of pH

3.3 Sample volume

To investigate the effect of sample`s volume, fixed amount of analyte was solved in different volumes up to 100ml. 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 Fig3 the less the concentration is, the more the recovery is obtained.

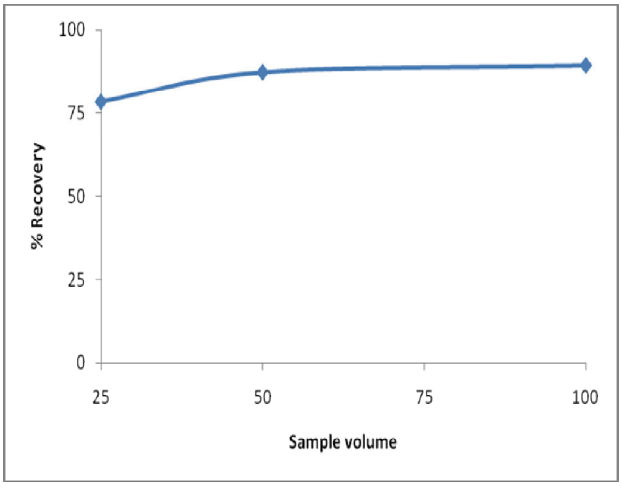


Fig 3: Effect of sample volume

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. The following figure show the comparison results obviously.

5 ANALYTICAL PERFORMANCE

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

Table 2: Linear equation, Correlation coefficient, Detection limit

Analyte	cefixime
Linear equation	y=10.57x-1456.4
Correlation coefficient	0.9957
Detection Limit	0.2μg/ml

The method was applied to analysis of tap water samples and the results are shown in table 3.

Table 3: Analysis of spiked water samples

Analyte	cefixime
Added (μg/l)	2.5
Found (μg/l)	2.19
Recovery (%)	87.6
RSD (%)(n=3)	0.90

6 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. Using small amount of sorbent is the positive point. The results showed that small amount of eluent are sufficient and when our samples were diluted better recoveries were concluded.

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