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Short communication

# Critical evaluation and comparison of enrichment efficiency of multi-walled carbon nanotubes, C18 silica and activated carbon towards some pesticides from environmental waters

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**Abstract**

In this work, optimization of multi-residue solid phase extraction (SPE) procedures coupled with high-performance liquid chromatography for the determination of Propoxur, Atrazine and Methidathion from environmental waters is reported. Three different sorbents were used in this work: multi-walled carbon nanotubes (MWCNTs), C18 silica and activated carbon (AC). The three optimized SPE procedures were compared in terms of analytical performance, application to environmental waters, cartridge re-use, adsorption capacity and cost of adsorbent. Although the adsorption capacity of MWCNT was larger than AC and C18, however, the analytical performance of AC could be made close to the other sorbents by appropriate optimization of the SPE procedures. A sample of AC was then oxidized with various oxidizing agents to show that ACs of various surface properties has different enrichment efficiencies. Thus researchers are advised to try AC of various surface properties in SPE of pollutants prior to using expensive sorbents (such as MWCNT and C18 silica).

*Keywords:* Activated carbon; Multi-walled carbon nanotubes; C18 silica; Solid phase extraction; Water samples; Pesticides

## 1. Introduction

Solid phase extraction (SPE) is the most common technique that is used for preconcentration of analytes in environmental waters [1]. In SPE procedure, the choice of appropriate sorbent is a critical factor to obtain full recovery and high-enrichment factor. Multi-walled carbon nanotubes (MWCNTs) have been recently used as preconcentrating sorbent for many organic pollutants [2–19]. On the other hand, activated carbon (AC) is an old sorbent [20], which has been extensively used for preconcentration and sample clean-up. Sometimes it is necessary to take into account the cost of adsorbent in addition to its analytical performance. This is of great importance especially when cheaper sorbent does the job with satisfactory analytical performance. This necessitates performing comparative studies among various sorbents and then deciding which sorbent is the cheapest with appropriate analytical performance.

There are very few comparative studies in the literature among various sorbents. For example, Zhou et al. [6] conducted a comparison of the enrichment efficiency among MWCNTs, AC and C18 silica as sorbents for SPE of Atrazine and Simazine in environmental waters. However, they did not specify the type, surface properties and textural characteristics of the AC used in their study [6]. They proposed that AC did not give the expected extraction efficiency because of its large size and blank volume and less active sites for adsorption. D'Archivio et al. [21] compared different sorbents (C18 silica, graphitized carbon black) and four different polymeric sorbents. Niu et al. [22] compared the enrichment efficiency of MWCNT with C18 silica towards phenolic compounds.

In this work, we report a comparison between AC with MWCNT and C18 silica as SPE sorbents for some pesticides from environmental waters prior to their simultaneous analysis by HPLC. This type of comparisons is rare in the literature. The pesticides involved are model pesticides that have been

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selected from various common pesticides' categories usually used in Jordan (viz. Atrazine "a triazine herbicide", Propoxur "a carbamate insecticide", Methidathion "an organophosphorus insecticide and acaricide"). One objective of this work is to reach a conclusion whether it is advantageous to use expensive sorbents (such as MWCNT and C18 silica) as SPE sorbent or not. To study the effect of surface properties of AC on its preconcentration efficiency, AC was oxidized by various sorbents to alter its properties.

## 2. Experimental

### 2.1. Chemicals

Atrazine, Propoxur and Methidathion standard material were kindly provided by Vegetarian and Agricultural Production Company/VAPCO (Al-Zarqa, Jordan) as 10 μg mL$^{-1}$ solution in acetonitrile. Working solutions were prepared daily by appropriate dilution of the stock solutions with water. Acetonitrile, water and methanol were all of HPLC-grade purchased from TEDIA, Ohio, USA. All other solvents and reagents used were of analytical reagent grade unless stated otherwise. Multi-walled carbon nanotubes (MWCNTs) were purchased from Shenzhen Nanotechport Co. Ltd., Shenzhen, China. MWCNT was of 1–5 μm length and 40–60 nm external diameter. It was treated with nitric acid to open the tube caps. Before use, MWCNTs were dried at 80 °C for 2 h. Specific surface area of the MWCNTs, as determined by $N_2$ adsorption, was provided by the manufacturer and found to be 40–300 m$^2$ g$^{-1}$. Activated carbon (AC) was purchased from Sigma (untreated granular activated charcoal, 20–60 mesh, product number C3014). C18 cartridges were purchased from Supelco.

### 2.2. Oxidation of the AC and characterization by Boehm titrations

AC was oxidized with various oxidizing agents to study the effect of oxidation on enrichment efficiency towards the target pesticides. Details of oxidation conditions are given in Table 1. Oxidized sorbents were thoroughly washed with doubly distilled water and then dried. The produced sorbents were labelled AC-NA, AC-HP and AC-APS, which refers to AC samples oxidized with nitric acid, hydrogen peroxide and ammonium per-sulphate, respectively. AC refers to the non-oxidized AC. The determination of surface oxides was described by Boehm [23].

### 2.3. Apparatus

SPE cartridge was prepared by placing the adsorbent in an empty 6 mL polypropylene SPE-tube "filtration tube" (from Supelco). Polyethylene frits (from Supelco) of 20 μm porosity were used to hold the adsorbent packing in the cartridge. Solid phase extraction process was performed using a visiprep-12-port vacuum manifold (from Supelco). The outlet tip of the manifold was connected to a vacuum pump (KNF NEUBERGER D-7800, Germany) and the flow rate was maintained at 6 mL min$^{-1}$.

HPLC analyses of the target pesticides (Propoxur, Atrazine and Methidathion) were performed using a model 785A programmable absorbance detector and a series 200 LC pump. Separations were performed on a spherisorb ODS2 (150 mm × 4.6 mm, 5 μm) from Dr. Maisch GmbH (Germany). A MetaGuard 2.0 mm Polaris 5 μ C18-A guard column was also used. The mobile phase consisted of acetonitrile and water (60/40 (v/v)), and the flow rate of the mobile phase was set at 1.0 mL min$^{-1}$. Chromatographic data were acquired and processed at 210 nm using a Perkin-Elmer 1022 LC Plus system.

### 2.4. General SPE procedure

0.200 g of the adsorbent was packed into the SPE-cartridge and pre-conditioned with 5 mL of acetonitrile then with 5 mL water ahead of the preconcentration procedure. Next, 50 mL of the water sample solution (spiked simultaneously with 50 ng mL$^{-1}$ of Atrazine, Propoxur and Methidathion and adjusted to pH 5) was passed through the cartridge. The cartridge was then washed with 5 mL of 10% acetonitrile aqueous solution to remove co-absorbed matrix materials. Subsequently, the retained Atrazine, Propoxur and Methidathion were eluted with 5 mL of acetonitrile. Twenty microliters of the eluent was injected into HPLC system for quantitative determination.

#### 2.4.1. Adsorption capacity

Adsorption capacity of the sorbents towards the three pesticides was estimated in separate experiments at pH 5 (optimum pH), by passing 50 mL of 5 μg mL$^{-1}$ of each pesticide solution

Table 1
Preparation conditions and surface oxides of AC sorbent with appropriate labelling of the oxidized adsorbents

| Adsorbent abbreviation | Oxidation conditions | Boehm titrations | | | | |
|---|---|---|---|---|---|---|
| | | a | b | c | d | e |
| AC | No oxidation | 1.46 | 0 | 0 | 0 | 0 |
| AC-NA | 100 mL of concentrated $HNO_3$, 25 °C, stirring for 24 h. | 0.121 | 2.164 | 0.613 | 0.563 | 0.988 |
| AC-APS | 100 mL saturated solution of $(NH_4)S_2O_8$ in 1 M $H_2SO_4$, 25 °C, stirring for 18 h. | 0.135 | 2.151 | 0.625 | 0.288 | 1.238 |
| AC-HP | Mixture of 50 mL $H_2O_2$ and 50 mL 1 M $H_2SO_4$, 50 °C, stirring for 1 h. | 0 | 2.051 | 0.838 | 0.438 | 0.775 |

a: total basic group (mmol g$^{-1}$), b: total acidic group (mmol g$^{-1}$), c: phenolic groups (mmol g$^{-1}$), d: lactonic groups (mmol g$^{-1}$), e: carboxylic groups (mmol g$^{-1}$).

Table 2
Summary of the experimental conditions of the three optimized preconcentration procedures using the adsorbents AC, MWCNT and C18 silica

| | Optimized SPE method using AC as sorbent | Optimized SPE method using MWCNT as sorbent | Optimized SPE method using C18 silica as sorbent |
|---|---|---|---|
| Breakthrough volume (mL) | 400 | 400 | 400 |
| Mass of adsorbent (g) | 0.300 | 0.200 | 0.400 |
| Washing solvent (mL) | 10 mL of 10% acetonitrile aqueous solution | 10 mL of 10% acetonitrile aqueous solution | 10 mL of 10% acetonitrile aqueous solution |
| Eluting solvent (mL) | 10 mL of acetonitrile | 10 mL of acetonitrile | 10 mL of acetonitrile |

(separately) into a 0.200 g of the sorbent packed in the cartridge and pre-conditioned as described above. The adsorbed pesticide was eluted with 20 mL acetonitrile to ensure full elution.

#### 2.4.2. Analytical performance of the method

Four hundred milliliters of highly purified (doubly distilled de-ionized) water samples were spiked with various concentrations of the three pesticides (simultaneously): 10, 17.5, 25, 37.5, 50, 75, 100 ng mL$^{-1}$ and then enriched using the desired sorbent according to the three optimized SPE procedures described in Section 3.1. SPE experiments were performed in five replicates ($n = 5$) and the five extracts were analyzed as separate samples.

### 2.5. Water samples

In this work, three types of environmental water samples were used for evaluation of the proposed SPE method; tap water, reservoir water and stream water; using grab sampling in borosilicate glass bottles. Tap water samples were taken after flowing for 10 min from various water taps in our school in different days, and then pooled and used to generate a composite tap water sample. Reservoir water composite sample was generated by collecting various samples from local household reservoirs; which are known to store water for several weeks. Stream water composite sample was generated by collecting various samples from Al-Zarqa stream from various positions at various days. Before use, all the environmental water samples were filtered through 0.45 μm micropore membranes and stored in brown glass bottles at 4 °C.

#### 2.5.1. Application of the proposed method on real water samples

Unspiked real water samples were analyzed according to the optimum SPE procedures. Since real water samples were free of the pesticides according to our procedure, water samples were spiked with the three pesticides (simultaneously) at various concentrations according to the estimated limit of linearity. SPE experiments were performed in five replicates ($n = 5$) and the five extracts were analyzed as separate samples.

## 3. Results and discussion

### 3.1. Optimization of SPE procedures

Optimization of SPE procedure using MWCNTs, C18 and AC involved the effect of pH of water sample, washing solvent and its volume, type of eluting solvent and its volume, mass of adsorbent, and breakthrough volume. Details of the optimization process are not presented here. However, a summary of the optimized parameters for simultaneous preconcentration of the three pesticides using MWCNT and C18 silica are given in Table 2. All the three sorbents gave optimum recovery at pH 5. It is noted that the only difference among the three optimized procedures was in the mass of adsorbent required in each procedure, i.e. mass of AC required is 0.300 g; mass of MWCNT required is 0.200 g; mass of C18 silica required is 0.400 g.

### 3.2. Comparing the performance of the three preconcentration procedures

#### 3.2.1. Analytical performance of the methods

Analytical parameters (linear range, detection limit, relative error range and precision) of the three SPE procedures are shown in Table 3. These results indicate that the precision of the optimized procedure by AC was very close to those obtained by the other two preconcentration procedures. The three preconcentration procedures have satisfactory precision at a very low level and the relative standard deviations %R.S.D. ($n = 5$) was always less than 4.0%. Linear ranges for the three target pesticides were estimated based on the value of the $r^2$ for the calibration curve. All the procedures were linear in the range 10–50 ng mL$^{-1}$ for the three pesticides. The detection limits of the three pesticides by the three optimized preconcentration methods were close to each other. They were estimated as three times the standard deviation of the blank signal. The relative error range of Atrazine and Propoxur in the three procedures were very close to each other, but the relative error range for Methidathion in case of AC was almost double that in the other two sorbents (MWCNT and C18 silica).

#### 3.2.2. Application of the method on real water samples

Three real environmental water samples (tap water, reservoir water and stream water) were used to validate and compare the three preconcentration methods using MWCNT, C18 silica and AC. The three target pesticides were not found in any of the real water samples by any of the three optimized methods. Thus the real water samples were spiked with the three pesticides (simultaneously) at various concentrations according to the appropriate linear ranges shown in Table 3 for each of the three optimized procedures. SPE experiments were performed in five replicates ($n = 5$) and the five extracts were analyzed as separate samples. Chromatograms from the SPE of spiked real waters using the

Table 3
Adsorption capacity of sorbents and analytical parameters ($n = 5$) of the three optimized preconcentration SPE procedures towards the target pesticides

| | Optimized SPE method using AC as sorbent | | | Optimized SPE method using MWCNT as sorbent | | | Optimized SPE method using C18 silica as sorbent | | |
|---|---|---|---|---|---|---|---|---|---|
| | Pr | At | Me | Pr | At | Me | Pr | At | Me |
| Adsorption capacity (mg $g^{-1}$) | 0.356 | 0.240 | 0.456 | 0.956 | 0.625 | 1.11 | 0.298 | 0.182 | 0.413 |
| Linearity range (ng $mL^{-1}$) | 10–50 | 10–50 | 10–50 | 10–50 | 10–100 | 10–50 | 10–100 | 10–50 | 10–50 |
| $r^2$ | 0.9722 | 0.9810 | 0.9997 | 0.9740 | 0.9990 | 0.9993 | 0.9947 | 0.9968 | 0.9986 |
| Detection limit (ng $L^{-1}$) | 230 | 94 | 23 | 220 | 58 | 36 | 193 | 78 | 33 |
| Precision, %R.S.D. range ($n = 5$) | 1.9–3.5 | 1.1–3.6 | 1.5–2.7 | 0.39–3.0 | 0.21–2.8 | 0.30–2.5 | 0.75–2.7 | 1.2–3.1 | 0.95–2.9 |
| Relative error range (%) | +1 to +8 | +3 to +11 | +9 to +18 | −3 to +10 | −2 to +10 | +2 to +8 | +1 to +10 | +2 to +7 | +5 to +10 |

Pr: Propoxur, At: Atrazine, Me: Methidathion.

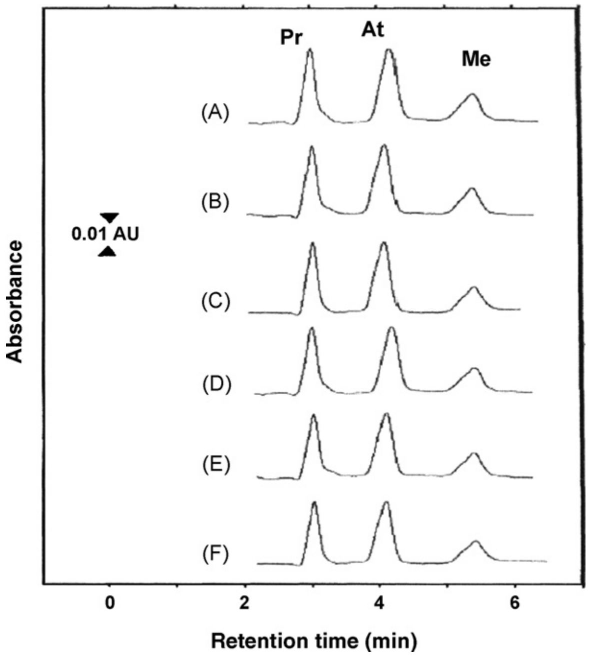

Fig. 1. Chromatograms from the three optimized SPE procedures of various environmental waters. A: reservoir water using MWCNT as sorbent, B: reservoir water using AC as sorbent, C: reservoir water using C18 silica as sorbent, D: tap water using AC as sorbent, E: stream water using AC as sorbent, F: tap water using MWCNT as sorbent. Peaks identification: Pr, Propoxur; At, Atrazine; Me, Methidathion.

three optimized SPE procedures (using AC, MWCNT and C18 silica) are presented in Fig. 1. Spike recoveries of the target pesticides in real water samples for each proposed method are shown in Table 4. It is noted that spike recovery range of the three pesticides with MWCNTs was 81–108%; with C18 silica was 60–95%; while with AC it was 70–98%.

### *3.2.3. Adsorption capacity and mass of adsorbent required in each optimum procedure*

From Table 2, it is noted that the only difference among the three optimized procedures lies in the mass of adsorbent required in each procedure, i.e. mass of AC required is 0.300 g; mass of MWCNT required is 0.200 g; mass of C18 silica required is 0.400 g.

The adsorption capacity of the three sorbents towards the pesticides is presented in Table 3. It is noted that adsorption capacity of the adsorbents was generally in the following order: MWCNT > AC > C18 silica. It is also noted that the adsorption capacity of MWCNT is almost three times that of AC and C18 silica. This explains why 0.300 g of AC and 0.400 g of C18 silica are needed to do the same job as 0.200 g of MWCNT.

### *3.2.4. Cost of adsorbent*

The price of C18 silica from ACROS is US$200 per 50 g, i.e. US$4 per gram. The average price of activated carbon from ACROS and Aldrich is US$75 per kg, i.e. US$0.075 per gram. The price of MWCNT varies from ∼US$20 per gram (from Aldrich) to ∼US$3 per gram (from Shenzhen Nanotechport Co.

Table 4
Spike recovery ranges of the three optimized preconcentration procedures of target pesticides in environmental waters

| | Optimized SPE method using AC as sorbent | | | Optimized SPE method using MWCNT as sorbent | | | Optimized SPE method using C18 silica as sorbent | | |
|---|---|---|---|---|---|---|---|---|---|
| | Pr | At | Me | Pr | At | Me | Pr | At | Me |
| Tap water | 82–90 | 70–90 | 81–91 | 86–96 | 91–101 | 85–96 | 92–94 | 93–95 | 85–95 |
| Reservoir water | 82–98 | 80–96 | 83–92 | 85–107 | 93–108 | 96–104 | 92–99 | 70–94 | 60–87 |
| Stream water | 82–91 | 70–87 | 81–87 | 82–102 | 81–105 | 81–101 | 72–94 | 70–89 | 73–85 |

Pr: Propoxur, At: Atrazine, Me: Methidathion.

Ltd., China). This means that MWCNT and C18 silica may be 250 times and 50 times as expensive as AC, respectively.

### 3.2.5. Cartridge re-use

Experimental results indicated that the three adsorbents may be re-used over 100 times after proper cleaning and re-conditioning. However, it is not always recommended to re-use the cartridge to avoid contamination and error in the results. Additionally, re-using the cartridge necessitates consuming substantial amounts of expensive solvents for cleaning the adsorbent. For the highly expensive MWCNT sorbent, it may be worthy re-using the cartridge, but not in case of cheap sorbents, such as activated carbon.

## 3.3. Comparing our results with the literature

Zhou et al. [6] conducted a comparison of the enrichment efficiency of MWCNTs, AC and C18 silica as the sorbents for SPE of Atrazine and Simazine in environmental waters. They proposed that “AC did not give the expected extraction efficiency because of its large size and blank volume and less active sites for adsorption”.

They did not show the type, surface and textural characteristics of the AC they used. It is recommended that researchers try AC of various chemical and textural properties in SPE of various analytes before attempting to use expensive sorbents. Our results reveal that there is a contradiction with the results obtained with Zhou et al. [6]. However, we would like here to state that adsorption characteristics of certain pollutants may vary with the surface chemistry and textural properties of AC. Thus changing the type of AC or altering the properties of AC may enhance or reduce adsorption of certain pollutants if the AC selected has appropriate properties for adsorption of those pollutants. For that purpose, it was considered reasonable to try altering the surface properties of AC by oxidation and then studying its effect on enrichment efficiency.

## 3.4. Effect of oxidation of AC

The aim of this section is to show that AC of various surface properties has different enrichment efficiencies. It is known [23] that oxidation of AC usually enhances the quantity of carboxyl groups on the surface of AC. Various oxidized AC sorbents (AC-NA, AC-APS and AC-HP) were used as a SPE sorbents at various pH values of the target pesticides. Results and details of the SPE experiments are shown in Fig. 2. Surface oxides of oxidized and non-oxidized ACs are presented in Table 1. It is generally noted that the non-oxidized AC and the oxidized ACs all gave the highest recoveries for the three pesticides (Propoxur, Atrazine and Methidathion) at pH 5. Comparing the percentage recovery when using the oxidized AC with the non-oxidized AC generally reveals that oxidation of the AC with various oxidizing agents reduced the recovery. This is probably due to carboxyl groups (formed upon oxidation of carbon surface) which tend to form water clusters on the micropores' openings in the AC surface [24] and thus blocking pesticides from entering the micropores. It is noted that the lowest recov-

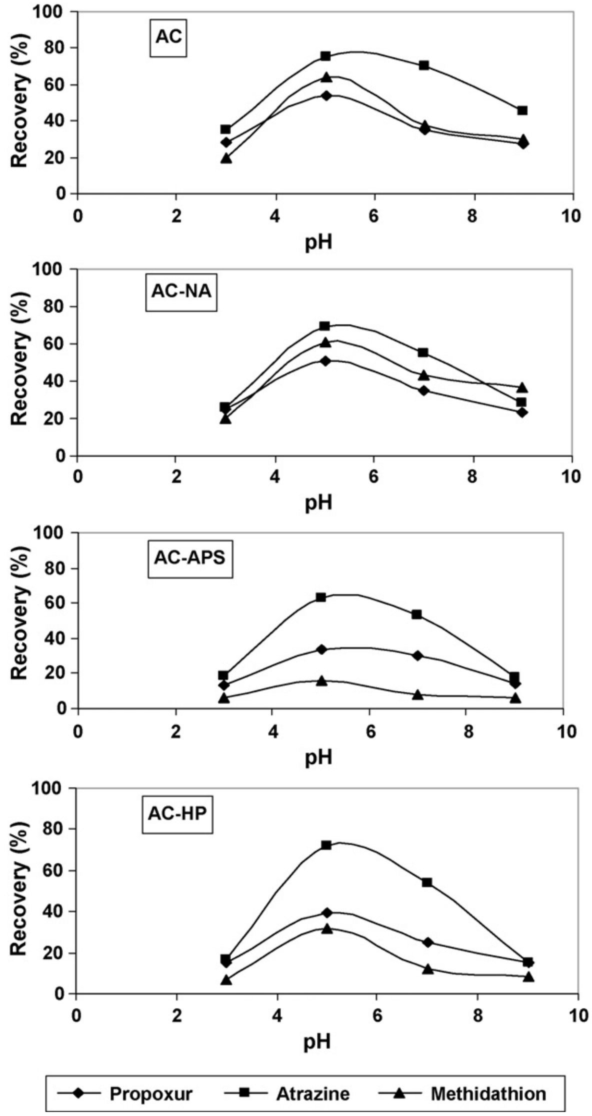

Fig. 2. Effect of oxidation of AC on percentage recovery of the pesticides from water at various pH values: 50 mL water sample spiked with 50 ng mL$^{-1}$ of the three target pesticides; 0.200 g adsorbent; washing solvent: 5 mL of 10% acetonitrile aqueous solution; eluting solvent: 5 mL of acetonitrile.

eries of the three pesticides were obtained when AC-APS was used as preconcentrating sorbent.

## 4. Conclusion

Using non-oxidized AC as preconcentrating sorbent in SPE of Propoxur, Atrazine and Methidathion gave satisfactory results when applied to environmental waters. Analytical performance was comparable to those obtained with MWCNTs and C18 silica. Although MWCNT has more adsorption capacity towards the selected pesticides, however AC is superior over the other sorbents in that it is much cheaper. Thus it is not always advantageous to use expensive sorbents in SPE of analytes. It is recommended that researchers try AC of various chemical and textural properties in SPE of various analytes before attempting to use expensive sorbents. There should be a balance between cost and benefits in using the proper sorbent. Studying the effect of AC oxidation on SPE process indicated that surface chemistry may have an effect on the SPE process. For example, the generation of carboxyl groups will form water clusters that block pore openings and hinder adsorption. Therefore, to enhance the enrichment performance of AC, authors should try AC of various textural properties and surface chemistry.

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