



Determination of Fluoxetine in Hospital Wastewater Using Solid-Phase Microextraction Fiber Coated With SWCNT

Mahdi Khoshnood¹, Mohammad Naimi-Joubani², Behzad Chahkandi³, Mahmoud Ebrahimi^{1*}

¹Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

²Research Center of Health and Environment, Department of Environmental Health Engineering, School of health, Guilan University of Medical Science, Rasht, Iran

³Department of Chemistry, Shahrood Branch, Islamic Azad University, Shahrood, Iran

*Correspondence to

Mahmoud Ebrahimi,
Department of Chemistry,
Mashhad Branch, Islamic
Azad University, Mashhad,
Iran
Email:
m.ebrahimi@mshdiau.ac.ir

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Abstract

Fluoxetine is used as an effective antidepressant in psychopharmacology. As a pharmaceutical and personal care product (PPCP) found in superficial waters, fluoxetine influences the wildlife that inhabit these waters. This study was conducted to determine the fluoxetine concentration even in trace quantity in the hospital wastewater, using a solid-phase microextraction (SPME) silica fiber layered with single-walled carbon nanotubes (SWCNTs). An instrumental setup including off-line SPME, which uses a simple carbon nanotube (CNT) to bond capillary column combined with fluorescence spectrometry, was arranged as a sensitive method for the quantification of fluoxetine in real sample. A one at-a-time optimization strategy was applied for optimizing extraction parameters such as extraction time, stirring rate, desorption time, pH, and salt effect on the extraction, pre-concentration and determination of fluoxetine in aqueous samples. The advantages of the developed method were: being simple to use with shorter amounts of time for analysis, lower equipment costs, thermal stability of fiber, and high relative recovery in contrast to conventional methods of analysis. Linear ranges were within 0.1-30 µg/L and the detection limit for the fluoxetine was 1×10^{-4} µg/L.

Keywords: Fluoxetine, Single-walled carbon nanotube, SPME, Silica fiber

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1. Introduction

Fluoxetine (N-methyl-c-[4-phenoxy]benzenepropanamine) is the first compound developed as a selective serotonin reuptake inhibitor (SSRI) and appears to be the most commonly approved antidepressant in the world (1). Pharmaceuticals and personal care products (PPCP) like fluoxetine are found in superficial waters and influence the wildlife that inhabit these waters (2). Fluoxetine is recommended for depression disorders in a daily dose of 20-80 mg and the therapeutic plasma concentration of fluoxetine ranges from 50 to 500 µg/L (3,4). Commercial drugs are usable. The concentration of combination of two fluoxetine enantiomers (S- and R-fluoxetine), which are approximately equipotent in absorbing serotonin, and are in circulation right now, is higher than that of parent drugs, while they are different in drug activities. In fact, S-norfluoxetine is about 20 times stronger than R-norfluoxetine as a serotonin inhibitor in-vitro and in-vivo (5).

Solid-phase microextraction (SPME) has been effectively applied in sampling and analysis of environmental samples, food, and pharmaceuticals.

Simplicity, solvent free nature, and easy coupling feature with gas chromatography (GC) and HPLC (high performance liquid chromatography) are some advantages of this technique (5-7).

Many commercial and laboratory-made SPME fibers have been developed for determination of the concentration of compounds in diverse presses; however, some disadvantages of the existing SPME fibers are: relatively low operating temperature, instability and swelling in organic solvents, easy to break, low extraction efficiency for polar compounds, and stripping off the coating (5). Progresses in SPME fibers as a highly efficient extraction procedure greatly depends on the discovery of new SPME fibers (5).

There are several procedures to fabricate the SPME fibers. For example, the dipping technique is applied for commercial production of SPME. It normally involves dipping a fiber in a solution containing organic solvent and materials to be deposited in the fiber. The commercially available SPME fibers are costly due to high costs of equipment (5). The performance of SPME

fibers improves simultaneous with the progresses in Nanomaterials (9,10). The carbon nanotubes (CNTs) with large surface areas, robust mechanical properties, and being chemically inert are the effective sorbent nanomaterials (11-16), which have been successfully used as the SPME fiber coating for the analysis of the organic compounds, such as phenols, polybrominated biphenyls, and organochlorine pesticides (17-19). Low thermal stability and swelling in the organic solvents occur due to lack of bonding between coating and substrate. In one study, the SPME fiber coated with single-walled carbon nanotubes (SWCNTs) was developed, which could successfully extract the organochlorine pesticides from wastewaters (19).

This study was conducted to fabricate and characterize SWCNTs/fused-silica fibers, based on the surface modification of both SWCNT materials and fused-silica fibers. Moreover, the efficiency of fabricated SWCNTs/SPME fibers in adsorbing fluoxetine from hospital wastewater was evaluated.

2. Materials and Methods

2.1. Chemicals and Materials

Chemicals including H_2SO_4 , HCl, NaOH, methanol, Triton x-100, 3-aminopropyltriethoxysilane (APTES), and acetone were of analytical grade and purchased from Merck (Darmstadt, Germany). Fluoxetine hydrochloride 98% was purchased from Sigma-Aldrich (St. Louis, USA). The stock solution (5000 $\mu\text{g/mL}$) of fluoxetine was prepared in HPLC-grade methanol and stored in the refrigerator at 4°C . Stock and working solutions of fluoxetine were prepared in methanol (1.0 mg/mL) and stored at -20°C , protected from light.

2.2. Apparatus

The spectrofluorometer used in this study was a Varian (CARY Eclipse, Australia) containing a photomultiplier tube (PMT) detector equipped with a xenon lamp, which was set at the wavelength of 190–800 nm. A fluorescent spectrum was recorded with the slit widths of 5 nm and at the excitation and emission wavelengths of 246 and 294 nm, respectively. Solutions were stirred by a Heidolph MR3001 magnetic stirrer (Schwabach, Germany) and a magnetic stirring bar (8 mm \times 1.5 mm). The microstructure of samples was investigated by scanning electron microscopy (SEM) (LEO, Model 1450VP, Germany). Fourier-transform infrared spectroscopy (FTIR) (Nexus 470, Thermo Nicolet, USA) was used to characterize the oxygen-containing functional groups in SWCNTs. A Metrohm 780 pH-meter (Herisau, Switzerland) equipped with a combined glass electrode was used to determine pH values during the experiment.

2.3. Environmental Sample Collection

The sanitary wastewater sample was collected from Sina hospital (Mashhad, Iran). This sample was filtered

through a 0.45 μm filter and stored at 4°C .

2.4. Silanization of Fiber Surface

The silanization procedure of the fiber surface was described similar to the silanization of fused-silica capillary (10,20). The capillary tube was cleaned by a mixture of hydrogen peroxide and concentrated sulfuric acid (35:65 v/v) to remove the protective polyimide layer (21), and then this part was dipped in a 1.0 M NaOH solution and heated in a hot water bath (70°C) for 30 minutes. Afterward, the fiber was placed in a dry tube and kept at 130°C for 30 minutes. Thereafter, it was rinsed with ultrapure water to achieve $\text{pH} = 7$, and then dried at room temperature. The hydroxylated part of the fiber was dipped in an APTES solution for 10 hours, at 120°C . These 2 operations were repeated for 6 cycles to form a silanized layer on the fiber. Finally, it was rinsed with toluene and ethanol, and dried at room temperature.

2.5. Preparation of SPME Fiber Coated With SWCNTs

To prepare SPME fiber, 200 mg of SWCNTs were refluxed in 20 mL mixture of concentrated nitric acid and sulfuric acid (1:3, v/v) at 130°C for 45 minutes. The mixture was washed with deionized water until $\text{pH} = 7$ and centrifuged and dried at 120°C for 4 hours. Then, 30 mg of the acid treated SWCNTs were dispersed in 5 mL of Triton x-100 with ultrasonication (300W, 40 kHz) and a suspension containing 2 mg/mL of SWCNTs was obtained (5). The fibers were immersed into SWCNT suspension for 24 hours and then dried at 120°C to remove the solvent. The SPME fibers coated with SWCNTs were oxidized by the mixture of H_2SO_4 and HNO_3 (v/v, 3:1) to create COOH groups at the sidewall of the SWCNTs. The prepared SPME fiber was characterized by FTIR and SEM.

2.6. SPME Procedure

Ten milliliters of aqueous sample were placed in a 15-mL vial and stirred by a shaker. The ionic strength and pH of the sample were adjusted with 0.1 M HCL and 0.1 mol/L NaOH. Extraction was performed at room temperature and with stirring rate of 1600 rpm. After extraction, 0.5 mL of acetonitrile was added to desorb the analyte from the fibers and then the fluorescence spectrum was recorded.

3. Results and Discussion

3.1. FTIR Spectrum of the SWCNT/SPME Fiber

To investigate the oxygen-containing functional groups on acid treated SWCNT sample, the FTIR spectrum of the sample was observed as shown in Fig. 1. The vibrational mode at $\sim 1500\text{ cm}^{-1}$ was corresponding to C=C bonds. Moreover, the peak at $\sim 1152\text{ cm}^{-1}$ resulted from C-O groups, and peak at $\sim 1726\text{ cm}^{-1}$ was assigned to carboxylic groups. The pretreated SWCNT presents absorption peaks at 1726 and 1500 cm^{-1} , indicating

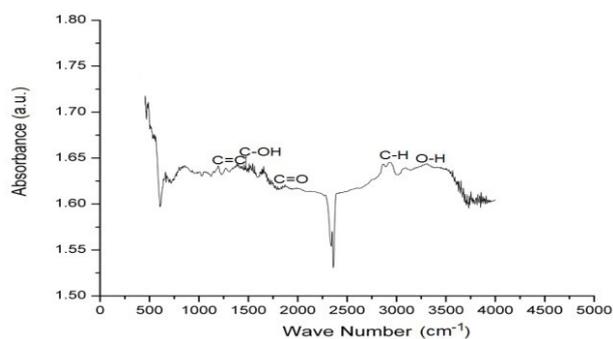


Fig. 1. Fourier-Transform Infrared Spectroscopy (FTIR) of Acid Treated SWCNTs.

the SWCNT carboxylic and carboxylate groups (22). Additionally, the peak at 1152 cm^{-1} could be ascribed to the stretching vibrations of O–H and C–OH.

According to the results of this study, acid treatment introduced oxygenated groups to the surface of CNTs, as confirmed in other studies (22,23).

Oxygen-containing functional groups on SWCNTs enhance the polarity of SWCNTs, and improve dispersion of SWCNTs in organic solvents such as DMF and Triton x-100. In addition, the acid-treated SWCNTs were negatively charged due to the occurrence of carboxylic groups (see Fig. 1).

The SWCNTs tended to assemble into bundles, making them difficult to disperse in the solution, due to the strong Van der Waals attraction forces between nanotubes (24). Although SWCNTs possessed oxygen-containing functional groups after acid treatment, more than 24 hours of ultrasonication was still required to obtain a stable SWCNT suspension in Triton x-100. The surface characteristic of the SWCNT-coated fiber was investigated by SEM. Figs. 2 and 3 show the coated fiber.

3.2. Experimental Optimization for the SPME

Various parameters affecting the extraction efficiency of fluoxetine in aqueous sample, including extraction time, salt effect, desorption time, stirring rate, and pH were studied and subsequently optimized.

3.2.1. Effect of pH

It is well known that the pH of donor solutions plays an essential role in the extraction of basic drugs. Analytes should be in their neutral form, in order that they could be extractable by the organic solvent in the fiber. Fluoxetine is a basic molecule with pKa of 10.05. The extraction efficiency of the fluoxetine using solution with different pH values from 2 to 11 was studied. As shown in Fig. 4, fluorescence intensity increased with the increase of pH value within the range of 2-5 and then decreased up to pH=7 and ultimately increased as the pH value increased. Further intensity was attained at pH=11. The main interactions between the SWCNT fiber and fluoxetine

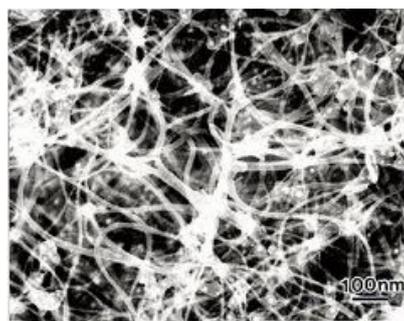


Fig. 2. Scanning Electron Microscopy Image of SWCNTs.

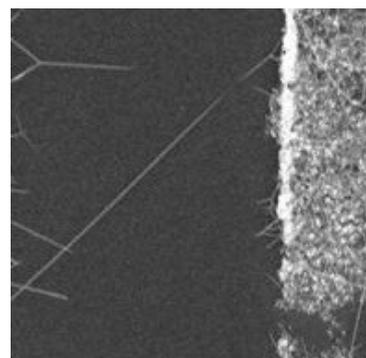


Fig. 3. Deposition of SWCNT on Silica Fiber

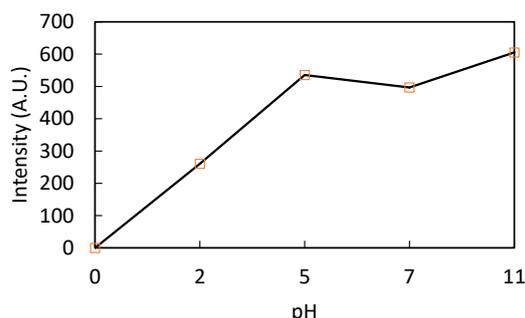


Fig. 4. The Effect of pH on the Fluorescence Intensity in the Presence of Fluoxetine. SPME conditions: Extraction time 20 min; desorption time 15 min; fluoxetine concentration $1\text{ }\mu\text{g/L}$.

were hydrophilic and hydrophobic interactions, and the ion exchange interaction probably had an insignificant role.

3.2.2. The Salt Effect

The ionic strength of the samples in SPME procedure can strongly affect the efficiency of the extraction procedure. The extraction efficiency of fluoxetine was increased with the addition of salt into sample matrix, particularly to more polar analytes through salting-out effect. The interaction of the analyte with added ions can reduce the diffusion of the analyte into the extraction phase. An increase in matrix viscosity can hinder the analyte mobility and affect the extraction efficiency; so,

salt effect was studied in a concentration range from 1% to 5%. It was observed that the fluorescence intensity of the analyte increased as the salt was raised to a concentration of 3%, and then decreased as the salt effect increased further (as shown in Fig. 5). Therefore, a concentration of 3% (w/v) was selected as the optimum salt concentration.

3.2.3. Effect of Stirring Rate

The magnetic stirring rate is most generally used in SPME experiments to enhance the extraction efficiency. It was shown that the intensity in fluorescent areas of the analyte increased as the stirring rate increased from 0 to 1600 rpm. Increasing the stirring rate up to 1600 rpm could result in massive air bubbles and decrease the pre-concentration factor (see Fig. 6); therefore, 1600 rpm was set as the optimum stirring rate for subsequent experiments.

3.2.4. Effect of Extraction Time

The extraction time is a significant factor in an SPME technique; it influences the partition of the analytes between sample solution and fiber coating. In this regard, extraction was done within 5- 55 minutes in order to assess the effect of extraction time on the extraction efficiency of fluoxetine. Four different extraction periods were tested (results presented in Fig. 7). Mass transfer is a process of diffusion through the pores in SWCNT; therefore, the porosity of SWCNT layer on the SPME

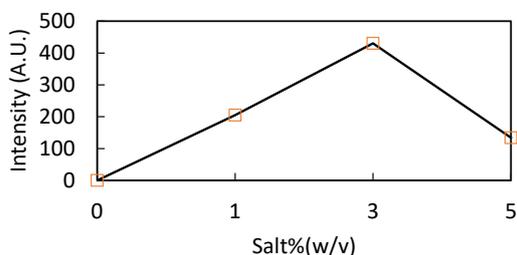


Fig. 5. The Effect of Salt on the Fluorescence Intensity in the Presence of Fluoxetine. SPME conditions: Extraction time 20 min; desorption time 15 min; fluoxetine concentration 1µg/L; pH=11.

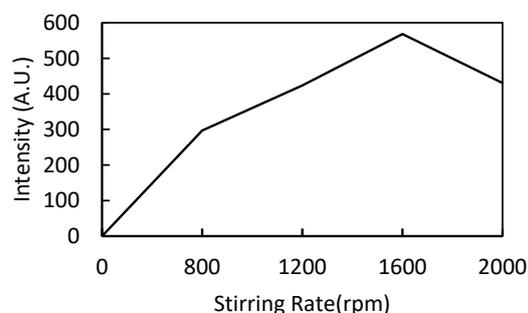


Fig. 6. The Effect of Stirring Rate on the Fluorescence Intensity in the Presence of Fluoxetine. SPME conditions: Extraction time 20 min; desorption time 15 min; fluoxetine concentration 1µg/L; pH=11; salt concentration 3% NaCl.

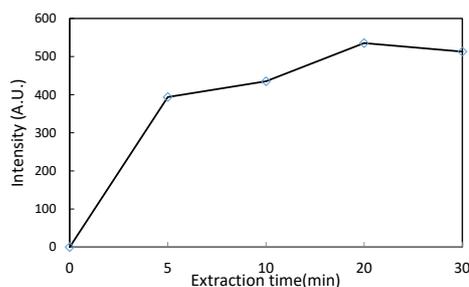


Fig. 7. The Effect of Extraction Time on the Fluorescence Intensity in the Presence of Fluoxetine. SPME conditions: Desorption time 15 min; fluoxetine concentration 1 µg/L; pH=11; salt concentration 3% NaCl; stirring rate 1600 rpm.

fiber can intensely affect the extraction dynamics. The extraction efficiency increased when the extraction time increased from 5 minutes to 20 minutes but did not reach the equilibrium, and then decreased as the extraction time increased further. Thus, 20 minutes was selected as the optimum extraction time considering the sensitivity and analysis speed.

According to the results obtained in this study, the maximum extraction efficiency of fluoxetine in aqueous solution was obtained using the fabricated SPME fiber under the following optimum conditions: extraction time, 20 minutes; desorption time, 15 minutes; desorption pH =11: and stirring rate, 1600 rpm.

3.3. Figures of Merit

Figures of merit in this method including correlation coefficient (R), experimental limit of detection (LOD), and linear dynamic range (LDR) were investigated under the best conditions. The method was applied to analyze the spiked sanitary wastewater sample with the recovery of 96.7%. The results are displayed in Table 1.

3.4. Sample Analysis

The established SPME–fluorescence method was used to determine the fluoxetine content in sanitary wastewater. Fig. 8 illustrates the chromatograms of the fluoxetine based on the SMPE method.

In order to investigate the performance of the established method, SWCNT fiber was applied to extract sanitary wastewater sample spiked at 5 µg/L. The recovery and precision is listed in Table 2. The relative recovery (RR) and RSD were 96.7% and 0.32%, respectively. The results showed that SWCNT fiber could be applied in the analysis of fluoxetine in hospital wastewater matrix.

Table 1. Figures of Merit in the Proposed Method for the Determination of Established SPME for the Extraction of Fluoxetine From Aqueous Solution

| Sample | LDR (ppm) | R ² | LOD (ppm) | RSD (%) |
|------------|-------------|----------------|-----------|---------|
| Fluoxetine | 0.0001-0.03 | 0.985 | ~0.0001 | 0.42 |

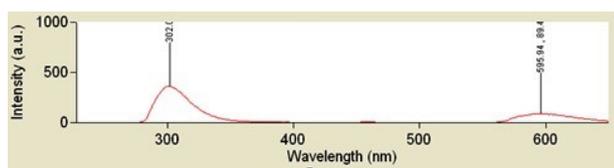


Fig. 8. Fluorescence Spectrum of Fluoxetine Based on SPME Method.

Table 2. Figures of Merit in the Proposed Method for the Determination of Fluoxetine in the Hospital Wastewater

| Sample | Relative Recovery (%) | RSD (%) |
|------------|-----------------------|---------|
| Fluoxetine | 96.7 | 0.32 |

4. Conclusions

In the present study, SWCNTs were treated with concentrated nitric acid to prepare fiber surfaces which could improve their capability in adsorbing the ions from solution. In the pre-concentration method, the use of SWCNT as a sorbent material for SMPE/spectrofluorescence was evaluated and demonstrated to be favorable for routine determination of trace/ultra-trace compounds. The adsorption behavior of the analytes on SWCNTs was investigated systematically.

The analytes remained on SWCNTs could be easily desorbed and no carryover was observed in the next analysis. It is expected that SWCNTs have great potential as an adsorbent in the pre-concentration and determination of trace/ultra-trace compounds in various samples.

Conflict of Interest Disclosures

The authors declare that they have no conflict of interests.

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