Novel magnetic solid-phase extraction using carboxylated multwall carbon nanotubes was proposed with ultra high-performance liquid chromatography–tandem mass spectrometry for the determination of silodosin in biological samples. The effects of various experimental parameters including adsorbent amount, pH, adsorption time, desorption conditions, and adsorbent reusability were systematically validated. Under the optimized conditions, the calibration curve was linear within the concentration range of 1.0–800 ng mL⁻¹ with the correlation coefficient of 0.9997 and the lower limit of detection was 0.3 ng mL⁻¹. The extraction recoveries were over 90.0% with relative standard deviation (RSD) of less than 5.0%. All these results suggested that magnetic extraction method can be used for enrichment and quantification of silodosin in biological samples.

**Keywords:** Silodosin, magnetic solid-phase extraction, multiwalled carbon nanotubes, biological samples, UPLC–MS/MS

**Introduction**

Benign prostatic hyperplasia (BPH) is one of the most common diseases in the male urogenital tract. At least 78% of men aged over 60 years have histological evidence of BPH [1]. Silodosin is a highly effective drug for symptomatic treatment of BPH [1]. Among these α-adrenoceptor antagonists, silodosin can effectively inhibit prostate contraction by acting on urinary bladder and prostatic urethra [2]. It is used to relieve and even treat the symptoms of lower urinary in elderly patients [3–5].

To date, several literatures have reported different detection methods of silodosin in pharmaceutical dosage forms and biological samples by the use of ultraviolet spectrophotometry [6], high-performance liquid chromatography (HPLC) [7, 8], ultra-high-performance liquid chromatography (UHPLC) [9], liquid chromatography–tandem mass spectrometry (LC–MS/MS) [10], and even electrochemical sensor method (ES) [11]. Based on the interference of the complex metabolites and complicated pretreatments in biological samples, it is necessary to determine silodosin by an appropriate adsorbent material for the enrichment.

The discovery of carbon nanotubes (CNTs) had brought an increasing number of researches because of their unique and alluring properties [12], such as excellent mechanical stiffness, nanoscale size, and high specific surface area [13]. Furthermore, magnetic materials of Fe₃O₄ nanoparticles (MNPs) as adsorbents have excellent magnetic response in comparison with traditional adsorbents and can be applied to many different fields such as chemical separation [14], analytical technique [15], immunodiagnosis [16], and tumor targeting therapy [17]. Without hazardous solvent extraction and additional evaporation, magnetic solid-phase extraction (MSPE) makes the separation operations convenient and efficient [18–28].

According to the best of our knowledge, magnetic solid-phase extraction of silodosin in biological samples has not been reported till date. In the present study, acid functionalized multiwalled carbon nanotubes coated by Fe₃O₄ (Fe₃O₄–MWCNTs–COOH) was used for effective adsorption and rapid determination of silodosin in human plasma and urine. Besides that, the effects of various experimental parameters were systematically validated by single factor design and extraction recovery of silodosin. The results indicated that the proposed method using Fe₃O₄–MWCNTs–COOH as an adsorbent exhibited good accuracy and repeatability in the silodosin extraction of biological samples.

**Experimental**

**Chemicals.** Multiwalled carbon nanotubes (MWCNTs) were purchased from Chinese Academy of Sciences (Chengdu, China). FeCl₃·6H₂O (99.0%, w/w) was obtained from Tianjin Zhiyuan Chemical Reagents Factory. All the other reagents in these experiments, such as nitric acid, sulfuric acid, ethylene glycol, sodium acetate, and ethane diamine, were of analytical grade without further depuration. Silodosin standard was provided by Jida Pharmaceutical Co. Ltd. (Kunming, China). Acetonitrile and methanol of HPLC grade were obtained from Merck (Darmstadt, Germany). Double-distilled water was purified with a Milli-Q purification system (Millipore, Bedford, MA, USA).

**Instruments and Apparatus.** Fourier transform infrared (FT-IR) measurements in the range of 4000–400 cm⁻¹ were carried out on a Shimadzu IRAffinity-1S Fourier transform infrared spectrophotometer by KBr disk. In addition, X-ray diffraction (XRD) analysis of Fe₃O₄–MWCNTs–COOH were recorded on a Rigaku D/max 2200 powder diffract meter (Tokyo, Japan) with Cu Kα radiation (40 kV, 35 mA). A JEM-100CXII (Japan Electronics) transmission electron microscope...
instrument was used to analyze the size and morphology of magnetic nanoparticles. The pH values of suspensions were determined with a digital pH-meter model PHS-3 (Shanghai, China) adjusted with hydrochloric acid or sodium hydroxide solutions.

**UPLC–MS/MS Conditions.** Chromatographic analysis and quantitative evaluation were performed using a Waters ACQUITY UPLC system (Waters, Milford, MA) which consisted of a controller and two pumps including a degasser and an autosampler. The analyte was detected using a Xevo TQD with Masslynx™ software (Version 4.1). The chromatographic separation was achieved on Waters ACQUITY UPLC BEH C18 column (50 mm × 2.1 mm, 1.7 μm). The column temperature was kept at 30 °C, and a small injection volume of 2 μL was recommended. The mobile phases consisted of water containing 0.1% formic acid (A), and acetonitrile (B) was used as gradient elute. Table 1 showed the UPLC gradient.

The samples were analyzed with an electrospray ionization set in the positive ionization mode (ESI+). Nitrogen was used as nebulization and desolvation gas. The multireaction monitoring (MRM) mode was operated by the dependent scan which was an enhanced product ion scan. The resulting transitions and setting for UPLC–MS/MS system are shown in Table 2. In order to develop maximum sensitivity for identification and detection of silodosin, the analyte specific parameters were set to 0.6 kV capillary voltage, 40 V cone voltage, 500 °C source desolvation temperature, 1000 L h⁻¹ source desolvation gas flow, and 50 L h⁻¹ cone gas flow.

**Preparation of Standard Solutions and Real Samples.** Standard stock solution of silodosin (100 μg mL⁻¹) was prepared in methanol and was stored in a fridge (4 °C). Working solutions were prepared directly by diluting the standard stock solution with methanol. Blood and urine samples were obtained from volunteers in the First People’s Hospital of Yunnan Province (Kunming, China). Appropriate stock solution of silodosin was spiked to the blank plasma and urine solutions. The concentrations of blood and urine samples were prepared with 10–100 ng mL⁻¹ of silodosin. All the solutions were stored at 4 °C.

To reduce the endogenous-related substances, the pretreatment procedure for blood and urine samples involves analogous steps. For the plasma preparation, 5 mL of blood samples was added to ethylenediaminetetraacetic acid (EDTA) as anticoagulant and centrifuged at 2000 rpm for 5 min; then, the supernatant solution was transferred to a 5-mL volumetric flask and diluted with water prior to MSPE procedure. For the urine samples, 5 mL urine was centrifuged at 3000 rpm for 5 min to eliminate the complex interference. Before the adsorption, the supernatant was collected and further diluted to 5 mL with water.

**Preparation of Fe₃O₄–MWCNTs–COOH Nanoparticles.** Synthesis of the magnetic nanoparticles was performed according to the previous literatures with some modifications [29, 30]. MWCNTs–COOH was synthesized as follows: 4 g of MWCNTs was cast onto mixed acid solution consisted of nitric acid (15 mL) and sulfuric acid (45 mL) and then sonicated for 3 h. Next, 100 mL of distilled water was dropped onto the solution as described above and centrifuged. Then, the resulting sediment was washed with distilled water thoroughly and finally dried in vacuum drying oven at 50 °C. FeCl₃·6H₂O (5 g) was added to 100 mL of ethylene glycol and dissolved; then, 360 mg acid functionalized MWCNTs were added under ultrasoundation for about 20 min. Next, 15 g of sodium acetate and 50 mL of ethane diamine were added and stirred for 20 min. Then, the black solution obtained was placed into Teflon-lined stainless-steel autoclave and heated at 200 °C for 8 h. The obtained Fe₃O₄–MWCNTs–COOH was collected with an external supermagnet, washed with ethanol, and distilled water for four times, and then, finally, vacuum-stowed at 45 °C for 12 h.

**MSPE Procedure.** The following steps were applied to extract and purify silodosin from sample solution: (1) 5 mL aliquot of samples were added into 10 mL polypropylene tube; (2) 20 mg of Fe₃O₄–MWCNTs–COOH was placed slowly into the solution; (3) after stirring gently for 1 min and adjusting pH value, the suspension was stationarily kept for 10 min; (4) Fe₃O₄–MWCNTs–COOH was gathered with a strong magnet, and the clear supernatant was carefully discarded; (5) in order to elute silodosin, 0.25 mL of methanol was gently dropped onto the magnetic sorbents, and then, Fe₃O₄–MWCNTs–COOH was separated by the magnetic field; (6) after filtration through a 0.22 μm membrane, the supernatant containing the target analyte was detected by UPLC–MS/MS. Figure 1 showed the procedure of silodosin extracted and collected in human biological samples by Fe₃O₄–MWCNTs–COOH.

**Results and Discussion**

**Characterization Results.** FT-IR spectrum absorption peaks of Fe₃O₄–MWCNTs–COOH were shown in Figure 2A. The strong and broad band around 3434 cm⁻¹ is attributed to the stretching mode of –OH in crystal water and MWCNTs of the common vibrated. A sharp characteristic peak of 1628 cm⁻¹ is associated with the stretching vibration of C=O in the –COOH groups. The weak bands at 1411 and 1401 cm⁻¹ are assigned to the bending vibration of –CH₂. Absorption peaks at 1092 and 876 cm⁻¹ are due to the –CH₃, –C=O–CH₂–, and C=O stretching vibration. The FT-IR spectrum of the Fe₃O₄–MWCNTs–COOH nanocomposite contains the characteristic peaks of Fe₃O₄ at 576 cm⁻¹. The results of FT-IR have shown that Fe₃O₄ NPs were successfully anchored onto the MWCNTs [31, 32].

X-ray diffraction (XRD) measurements were employed to investigate the phase purity and crystal structure of the synthesized Fe₃O₄–MWCNTs–COOH (Figure 2B). The main diffraction peaks of Fe₃O₄ are 30.20°, 35.52°, 43.34°, 53.82°, 57.32°, and 62.88°, and these values are corresponding to the planes (111), (200), (220), (311), (400), and (422), respectively. The results of XRD have shown that Fe₃O₄–MWCNTs–COOH are well matched with Fe₃O₄. It demonstrates that MWCNTs were successfully coated onto the Fe₃O₄ nanoparticles.

The morphological structure of Fe₃O₄–MWCNTs–COOH nanomaterial was investigated by transmission electron microscope (TEM) images. Different scales TEM images of Fe₃O₄–MWCNTs–COOH were shown in Figure 2 (C1 and C2), respectively. It clearly shows that the homogeneous structure of

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**Table 1. UPLC gradient for the analysis of silodosin**

| Time (min) | Flow rate (μL min⁻¹) | Mobile phase A (%) | Mobile phase B (%) |
|-----------|---------------------|--------------------|--------------------|
| 0.0       | 0.4                 | 80.0               | 20.0               |
| 2.0       | 0.4                 | 80.0               | 20.0               |
| 2.1       | 0.4                 | 10.0               | 90.0               |
| 2.5       | 0.4                 | 10.0               | 90.0               |
| 2.6       | 0.4                 | 80.0               | 20.0               |
| 3.0       | 0.4                 | 80.0               | 20.0               |

**Table 2. The three resulting MRM transitions and corresponding settings**

| Analyte   | Parent (m/z) | Daughter (m/z) | Cone voltage (V) | Collision energy (eV) | Remark      | Figure |
|-----------|--------------|----------------|------------------|-----------------------|-------------|--------|
| Silodosin | 496.23       | 244.16         | 38.0             | 24.0                  | Qualifier   |        |
| Silodosin | 496.23       | 479.28         | 38.0             | 16.0                  | Qualifier   |        |
| Silodosin | 496.23       | 261.26         | 38.0             | 28.0                  | Quantifier  |        |

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Fe$_3$O$_4$–MWCNTs–COOH and the determined particle size in the case of Fe$_3$O$_4$–MWCNTs–COOH were identified in the range of 40–200 nm. The TEM image showed the octahedron Fe$_3$O$_4$ nanoparticles growing on the MWCNTs surface regularly with uneven diameters and most of the Fe$_3$O$_4$ nanoparticles were strung by MWCNTs.

The possible interactions between the carbon surface and the phenols have been proposed by Laszlo: (1) electron donor–
acceptor interactions between the phenolic ring of silodosin and the basic surface oxygen of carbonyl groups in the carboxyl groups; (2) dispersion effect between the phenolic ring and the π electrons of the graphitic structure; and (3) electrostatic attraction and repulsion when ions are present [35, 36]. As a result, the mechanism of silodosin adsorption is determined by so-called “π–π” interactions and “donor–acceptor complex” formation. Carboxylic groups on the surface of MWNTs extract electron density from the basal planes of carbon and weaken π–π dispersion forces between the phenolic ring of silodosin and the graphitic structure of MWNTs.

Optimization of the MSPE Procedure. Experimental parameters including adsorbent amount, pH, adsorption time, desorption conditions, and adsorbent reusability were optimized for quantitative recoveries of silodosin on Fe₃O₄–MWCNTs–COOH. All experiments were performed in triplicate by varying a parameter on the retention efficiency.

Effect of the Adsorbent Amount. To test the effect of the adsorbent dosage, various amounts of magnetic Fe₃O₄–MWCNTs–COOH from 5 to 30 mg were added into sample solution containing 50 ng mL⁻¹ silodosin. The results in Figure 3 indicated that the recoveries of the analyte were greater than 90.0% by using 20 mg of magnetic nanoparticles. Also, with the continued increase of adsorbent amount, the recovery rate did not increased significantly. Consequently, the adsorbent dosage was maintained at 20 mg in all the subsequent experiments.

Effect of Solution pH. The pH value of the sample solution plays an important role due to changes in the partition coefficient of analyte between aqueous solution and the extraction solvent. To study the effect of the sample pH, the pH values were adjusted within a range between 3 and 10 by 0.1 M HCl or NaOH solution. As shown in Figure 4, the recoveries of silodosin increased as the pH of the sample solutions containing 50 ng mL⁻¹ silodosin increased from 2 to 7. However, the recoveries of silodosin were decreased slightly from pH 8 to 11. Since the pH of the plasma and urine samples was generally around 7, it is unnecessary to adjust the pH of the sample solutions.

Effect of Adsorption Time. A certain extraction time is required after the adsorbents and pH are dispersed into the solution in order to facilitate the interaction between analyte and Fe₃O₄–MWCNTs–COOH. The effect of adsorption times in range of 2 to 14 min was examined. The adsorption experiments were carried out at different time intervals, which were 2, 4, 6, 8, 10, 12, and 14 min, separately and respectively. It was observed that, after 10 min, the recoveries of silodosin had no significant variation (Figure 5). It may be due to the fact that the interaction of adsorption between the analyte and adsorbents was easily achieved in only 10 min, and a prolonged time did not contribute more enhancement of efficiency. According to the results, an equilibration time of about 10 min was required for quantitative extraction of the analyte from solution into the MNPs.

Effect of Desorption Conditions. An ideal elution solvent should be strong enough to elute all the target compounds from the sorbent. In our study, five common organic solvents alone or mixture including 20% acetonitrile (v/v), 20% methanol (v/v), ethanol, acetonitrile, and methanol were investigated. The results revealed that the better recoveries were obtained using methanol, which was due to the higher solubility of methanol than other solvents (Figure 6). The effect of eluent volume from 0.1 to 0.5 mL in the interval of 0.1 mL was also
observed, and 0.25 mL of methanol was adopted as the optimum eluent solvent in the follow-on experiments.

**Reusability of the Adsorbent.** In sorption-based investigations, sorbent reusability is economically assumed as a fundamental feature, whereby the spent sorbent could be reused several times. In order to assess the regeneration capacity, the sorbents of Fe₃O₄–MWCNTs–COOH can be reused up to four times without a significant loss of the extraction efficiency (Figure 7). This reflects that silodosin adsorbed onto sorbents was dependent on the surface chemical nature. On the other hand, the nanoparticles had a lamellar structure so that lamellar surface adsorbed other compounds and silodosin; thus, it made desorption of silodosin more difficult and led to the decrease of the adsorption efficiency. For higher extraction rate and higher efficiency, Fe₃O₄–MWCNTs–COOH is suitable for using no more than four times as an ideal solid-phase extraction material.

**Maximum Adsorption Capacity.** The capacity of the adsorbent is an important factor because it determines how much adsorbent is required to quantitatively remove a specific amount of silodosin from biological samples. In order to evaluate the maximum adsorption capacity, a standard solution containing 0.4 mg mL⁻¹ of silodosin was used, and the maximum capacity was calculated. Maximum adsorption capacities for silodosin were 26.3 mg g⁻¹.

**Analytical Figures of Merit.** The analytical characteristics of the optimized method were summarized in Table 3, including regression equation, linear dynamic range, correlation coefficient (r), limit of detection (LOD), repeatability, and enrichment factor. Enrichment factor (EF) was calculated as EF = K2/K1, where K2 (148,773) is the slopes of the calibration curves with extraction procedure, K1 (7743) is the slopes of the calibration curves without extraction procedure. Thus, an enrichment factor of about 19 was achieved using this procedure.

![Figure 7. Effect of reuse times](image)

**Figure 7. Effect of reuse times**

**Table 3.** The effect of potential interfering compositions in the determination of silodosin

| Interference                  | Interferent to analyte ratio (w/w) | Recovery (%) | RSD (%) |
|------------------------------|-----------------------------------|--------------|---------|
| Sodium chloride              | 2000:1                            | 97.8         | 2.1     |
| Lactose                      | 1000:1                            | 98.4         | 3.6     |
| Mannitol                     | 800:1                             | 95.6         | 2.5     |
| Ethylparaben                 | 800:1                             | 96.7         | 4.0     |
| Ketocconazole                | 500:1                             | 98.2         | 2.4     |
| Tamsulosin hydrochloride     | 500:1                             | 97.5         | 3.8     |

**Table 4.** Analytical performance data for silodosin by the MSPE technique (n = 6)

| Analyte          | Calibration equation | Linear range (ng mL⁻¹) | r       | RSD (%) | LOD (ng mL⁻¹) | LOQ (ng mL⁻¹) | Enhancement factor |
|------------------|----------------------|------------------------|---------|---------|---------------|---------------|-------------------|
| Silodosin        | Y = 148773X – 847    | 1.0–800                | 0.9997  | 2.1     | 0.3           | 1.0           | 19                |

**Selectivity of the Method.** To demonstrate the selectivity of the developed MSPE method for the preconcentration and determination of silodosin, some commonly used excipients in pharmaceutical formulations and some drugs on the determination of 50 ng mL⁻¹ silodosin were studied. A 2000-fold mass excess of them over silodosin was tested as the maximum ratio in Table 3. All solutions were operated under the optimal conditions with the same method. The tolerance limit was taken as the concentration of the interfering components causing a variation in the intensity of silodosin within ±5%. According to the obtained results, the developed method was free from the interference of usual excipients and analogues.

**Validation of Method.** Analytical performance of the developed procedure was plotted in Table 4. Calibration curves via plotting peak intensity of each concentration versus associated concentrations of the analytes were obtained. The method was linear in the range from 1.0 to 800 ng mL⁻¹, giving a regression coefficient (R²) of 0.9997. The limit of detection (LOD) for silodosin, calculated on the basis of three times the standard deviation of the blank readings by the slope of the calibration curve, was 1.0 ng mL⁻¹. As shown in Table 5, repeatability (inter-day, n = 6) and reproducibility (intra-day, n = 6) of the method at 10–100 ng mL⁻¹ level of the analyte were less than 4.3% and 3.9%, respectively. For estimation of

**Table 5.** Precision and accuracy for the detection of silodosin in urine and plasma samples

| Biological samples | Spiked (ng mL⁻¹) | Inter-day (n = 6) | Intra-day (n = 6) |
|--------------------|------------------|-------------------|-------------------|
|                    | Mean accuracy (%) | RSD (%)           | Mean accuracy (%) | RSD (%)           |
| Plasma             |                  |                   |                   |
| 10                 | 91.4             | 4.2               | 90.8              | 3.4               |
| 50                 | 97.7             | 2.7               | 95.2              | 2.2               |
| 100                | 92.1             | 3.3               | 94.0              | 2.1               |
| 10                 | 98.1             | 4.0               | 97.2              | 2.7               |
| Urine              |                  |                   |                   |
| 50                 | 95.6             | 4.3               | 96.0              | 3.9               |
| 100                | 95.6             | 3.4               | 94.1              | 2.5               |

**Table 6.** Stability of silodosin in plasma and urine samples

| Biological samples | Nominal concentration (ng mL⁻¹) | Calculated concentration (ng mL⁻¹) | RSD (%) |
|--------------------|---------------------------------|-----------------------------------|---------|
| Plasma             |                                 |                                   |         |
| 10                 | 9.48                           | 26.8                             | 2.3     |
| 50                 | 46.53                          | 63.1                             | 1.8     |
| 100                | 94.62                          | 111.2                            | 2.7     |
| Urine              |                                 |                                   |         |
| 10                 | 9.65                           | 47.8                             | 3.4     |
| 50                 | 48.08                          | 58.4                             | 1.5     |
| 100                | 95.73                          | 106                              | 2.0     |

**Table 7.** Recovery for silodosin from plasma and urine samples

| Biological samples | Added (ng mL⁻¹) | Found (ng mL⁻¹) | Recovery (%) | RSD (%) |
|--------------------|-----------------|-----------------|--------------|---------|
| Plasma 1           | 10              | 26.8            | 94.0         | 2.4     |
| 50                 | 63.1            | 91.4            | 3.5          |
| 100                | 111.2           | 93.8            | 1.3          |
| Plasma 2           | 10              | 21.4            | 93.0         | 4.2     |
| 50                 | 58.4            | 92.6            | 2.5          |
| 100                | 106             | 93.9            | 3.0          |
| Urine 1            | 50               | 47.8            | 95.6         | 2.2     |
| 100                | 95.5            | 96.3            | 2.0          |
| Urine 2            | 10              | 9.4             | 94.0         | 1.8     |
| 50                 | 48.7            | 97.4            | 2.4          |
| 100                | 95.5            | 95.5            | 3.7          |

*Not detected.*
stability of the processed samples, three spiking levels of samples were extracted. The MSPE samples at each concentration level were maintained at room temperature for 12 h before analysis. As shown in Table 6, sample stability results showed that the calculated concentrations for samples were all within ±10.0% of the nominal concentrations, indicating that samples were stable under normal laboratory conditions without significant loss of compound. The results showed that the MSPE method based on new magnetic sorbent is sensitive, efficient, and reliable along with good analytical parameters in isolation of silodosin from biological samples.

Analysis of Real Samples. To explore the reliability of the presented method, it was successfully applied to determine silodosin in biological samples including human plasma and urine samples. The results summarized in Table 7 showed that silodosin of recovery range from 91.4% to 97.4% were satisfactorily obtained using the proposed method. As shown in Figure 8, no significant matrix effect was observed for the real samples studied and the method offers acceptable accuracy. Analyte can be easily discriminated and quantified, since no conspicuous interference of the nearby components was observed in the quantitative analysis of silodosin. Table 8 compared analytical data between the proposed method and previous works for analysis of silodosin. The comparison of results showed that the proposed method has lower LOD and less extraction time with other reported methods.

Table 8. Comparison of different analytical methods used in determination of silodosin

| Instrument          | Matrix   | Extraction method          | Linearity range | LOD          | Extraction time (min) | Reference |
|---------------------|----------|----------------------------|-----------------|--------------|-----------------------|-----------|
| HPLC                | Capsules | Liquid extraction          | 10–30 µg mL⁻¹   | –            | –                     | 4         |
| RP-HPLC             | Tablets  | Liquid extraction          | 10–60 µg mL⁻¹   | 5.46 µg mL⁻¹ | –                     | 5         |
| UPLC                | API      | Liquid extraction          | 0.25–1.5 µg mL⁻¹| 80 ng mL⁻¹  | –                     | 6         |
| HPLC–MS/MS          | Plasma   | Liquid–liquid extraction  | 0.50–50 ng mL⁻¹ | 0.15 ng mL⁻¹| >20                   | 7         |
| ES                  | Capsules | Liquid extraction          | 5–1650 ng mL⁻¹  | 1.9 ng mL⁻¹ | –                     | 8         |
| UPLC–MS/MS          | Plasma and urine | Magnetic solid-phase extraction | 1.0–800 ng mL⁻¹ | 0.3 ng mL⁻¹ | 20 This work        |           |

*aActive pharmaceutical ingredients.*

Figure 8. Mass chromatograms of blank and spiked samples: (a) blank plasma sample; (b) plasma sample spiked with 50 ng mL⁻¹ of silodosin; (c) blank urine sample; (d) urine sample spiked with 50 ng mL⁻¹ of silodosin

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| ES                  | Capsules | Liquid extraction          | 5–1650 ng mL⁻¹  | 1.9 ng mL⁻¹ | –                     | 8         |
| UPLC–MS/MS          | Plasma and urine | Magnetic solid-phase extraction | 1.0–800 ng mL⁻¹ | 0.3 ng mL⁻¹ | 20 This work        |           |

*aActive pharmaceutical ingredients.*
Conclusions

In the present work, an easy and fast analytical method based on magnetic solid-phase extraction (MSPE) combined with UPLC–MS/MS has been developed. Acid functionalized multi-walled carbon nanotubes coated by Fe₃O₄ (Fe₃O₄–MWCNTs–COOH) were firstly used as sorbent of MSPE and successfully applied to the extraction and preconcentration of silodosin. The main advantages of the proposed method are that it is convenient, effective, and environmental friendly and that it can be successfully applied to biological samples without interfering effects. It is also expected that the Fe₃O₄–MWCNTs–COOH magnetic nanoparticles have a great potential application for analysis of drugs in human biological samples in a multipurpose extraction procedure.

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