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Magnetic solid-phase extraction based on methylcellulose coated-Fe_3O_4–SiO_2–phenyl for HPLC–DAD analysis of sildenafil and its metabolite in biological samples

Minqiong Tang [a], Qing Wang [a], Ming Jiang [a], Li Xu [a], Zhi-Guo Shi [b,*], Ting Zhang [c], Yan Liu [c]

[a] Tongji School of Pharmacy, Huazhong University of Science and Technology, Wuhan 430030, China
[b] Key Laboratory of Analytical Chemistry for Biology and Medicine, Wuhan University, Wuhan, China
[c] Institute of Oceanographic Instrumentation, Shandong Academy of Sciences, Qingdao 266001, China

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ABSTRACT

In the present study, magnetic nanoparticles (MNPs) with phenyl functionalized core and a hydrophilic methylcellulose coating were synthesized. The functionalized MNPs showed excellent dispersibility in aqueous solution and they were applied to magnetic solid phase extraction (MSPE) of sildenafil and its metabolite, desmethyl sildenafil, from human urine and plasma samples followed by high performance liquid chromatographic analysis. The factors that may influence the extraction, including the amount of MNPs, pH and salt concentration of sample solution, extraction and desorption time, and the volume of desorption solvent, were investigated in detail. Under the optimum MSPE conditions, the developed method showed satisfactory reproducibility with intra-day and inter-day relative standard deviations less than 8.2% and low limits of detection of 0.41–0.96 ng mL^{-1} from urine and plasma samples. The proposed material possessed good water compatibility and demonstrated excellent applicability for biological samples.

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1. Introduction

Magnetic solid-phase extraction (MSPE), a new type of solid-phase extraction (SPE) based on the use of magnetic particles [1] as the adsorbent, is an excellent sample pretreatment method with high extraction efficiency and convenient operation. Fe_3O_4 or γ-Fe_3O_4 magnetic nanoparticles (MNPs) are usually used as the core of sorbents [1,2], which makes isolation of the sorbents from the sample solution convenient once an exterior magnetic force is introduced; work efficiency is thus enhanced as this procedure avoids column packing and possible blockage in the case of traditional column SPE [2]. In addition, owing to its nano nature, MNP possesses large specific surface area, and the equilibrium time between the sorbents and sample solution is thus greatly shortened, resulting in relatively higher extraction capacity and detection sensitivity.

Bare MNPs were seldom directly used for extraction as they lacked functional groups to interact with the analytes. Alternatively, the functionalized MNPs, such as C_{18} [3,4] or C_8 alkyl chain, cation or anion exchange groups [5,6], graphene [4,7] and molecularly imprinted material [8–10] modified MNPs, were more frequently used. The applications were extended to pharmaceuticals [4,11,12], inorganic ions [13–15], pesticides [16–18], proteins [10] and DNA [19,20] in various sample matrices. However, extraction performance was unsatisfactory for functionalized MNPs with high hydrophobicity. Taking C_{18}-MNPs as an example, due to their hydrophobic nature, C_{18}-MNPs were difficult to disperse in aqueous solution which may influence their stability and deteriorate the extraction capacity further on [21]. As an efficient solution to this problem, multi-functionalized MNPs with good aqueous compatibility were put forward. As a typical example, the hydrophobic core with the hydrophilic external coating could be constructed on MNPs, which played the role for extraction and aqueous dispersibility, respectively. For instances, Cai et al. coated chitosan on the surface of C_{18}-MNPs as the MSPE sorbent [21,22] to extract perfluorinated and phthalate ester compounds from environmental water samples. Satisfactory extraction performance was obtained. In addition, non-ionic surfactants, i.e. Span and Tween [23], were compared to coat the C_{12}-MNPs to extract steroid hormones from environmental and biological samples by our group. Tween-20 and Tween-40 showed better water compatibility than the other studied Span and Tween surfactants. The additional hydrophilic coatings for this purpose included, polyethylene glycol [24], protein bovine serum albumin [24] and alkanethiolates [25], etc. Although this topic is attracting attention, the category of multi-functionalized MNPs are still

* Corresponding author. Tel.: +86 27 68752701; fax: +86 27 68754067.
E-mail address: shizg@whu.edu.cn (Z.-G. Shi).

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limited; it deserves further study to develop this kind of MNPs of easy preparation, high extraction efficiency and stable occurrence.

In the present work, a novel MNP which consisted of the internal phenyl surface (Fe_3O_4–SiO_2–Ph) and methylcellulose (MC) coating (Fe_3O_4–SiO_2–Ph–MC) was proposed. The phenyl groups rendered the material suitable for extraction of relatively polar analytes. MC possessed abundant hydrophilic hydroxyl groups, which was self assembled on the Fe_3O_4–SiO_2–Ph and supposed to improve water compatibility of the material.

Sildenafil (SD) is a typical phosphodiesterase-5 inhibitor which is abused as drugs and health products to treat male erectile dysfunction [26,27]. Adverse effects, such as headache, vertigo, the reduction of blood pressure and aggravation of cardiovascular disease, were found to be related to this compound. Hence, to monitor SD and its metabolites in biological samples for clinical or forensic purpose is of great significance. Herein, SD and its metabolite, desmethyl sildenafil (DD), were studied as target analytes. Determination of them in biological samples was realized through MSPE based on Fe_3O_4–SiO_2–Ph–MC as the sorbents followed by high performance liquid chromatographic (HPLC) analysis.

2. Experimental

2.1. Chemical and reagents

The SD and DD, whose structures were depicted in Fig. 1, were purchased from Aladdin (Shanghai, China). Methanol (MeOH) was supplied by Merck (Darmstadt, Hessen, Germany). Toluene, MC (M450), acetic acid (HAc), sodium chloride (NaCl), ethanol (EtOH), sodium acetate (NaAc), sodium hydroxide (NaOH), ethylene glycol (EG), polyvinyl alcohol (PVA) and ammonia ($NH_3 \cdot H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Triethoxysilane (TEOS) and phenyltrichlorosilane were obtained from Hubei Wuhan University Silicone New Material Co., Ltd. (Wuhan, China). Hydrochloric acid (HCl) was purchased from Kaifeng Dong Da Chemical Reagent Co., Ltd. (Henan, China). Pyridine was purchased from Tianjin Taixing Chemical Reagent Co., Ltd. (Tianjin, China). Ultrapure water was produced by a Heal Fore NW system (Shanghai, China).

2.2. Apparatus

Determination of SD and DD was performed on a Shimadzu (Tokyo, Japan) HPLC system, which consisted of two LC-20AD pumps, an SIL-20A autosampler, and an SPD-M20A photodiode array detector. Data were collected and processed by the Shimadzu LCsolution software. Chromatographic separation was performed on a DIONEX ODS (2.1 mm × 150 mm, 2.2 μm) column (Sunnyvale, USA) at a temperature of 30 °C. A mixture of MeOH and 1% HAc solution (62:38, v:v) was used as mobile phase at a constant flow rate of 0.1 mL min^{-1} and the injection volume was 10 μL. The detection wavelength was fixed at 290 nm for quantification. All the experiments were performed at least in triplicate.

The pH values were measured with a Mettler Toledo Delta 320 pH meter (Shanghai, China). Thermogravimetric analysis (TGA) was performed on an SETSYS-16 TG/DTA thermal analyzer (Setaram, France). Scanning electron microscopy (SEM) was carried out using a JSM-35CF instrument (JEOL, Tokyo, Japan). Fourier transform infrared (FTIR) spectroscopic experiment was carried out on a Nicolet (Madison, WI, USA) Impact 420 apparatus.

2.3. Sample preparation

Stock solutions, 1 mg mL^{-1} for the two analytes, were separately prepared in MeOH and stored at 4 °C. Aqueous samples were freshly prepared by spiking purified water with the analytes at a known concentration (0.2 μg mL^{-1}) daily to optimize extraction performance as specified.

Human plasma was collected from the clinical laboratory of Tongji Hospital (Wuhan, China), and the urine sample was obtained from a volunteer. They were stored at −80 °C before usage. The above samples without any pretreatment were adjusted to the desired pH value and were subjected to the extraction process as optimized. The blank plasma and urine samples were subjected to the same pretreatment procedures.

2.4. Preparation of Fe_3O_4–SiO_2–Ph–MC MNPs

The preparation procedure included three steps. (1) Synthesis of Fe_3O_4 nanoparticles [28]. Fe_3O_4 nanoparticles were synthesized by the solvothermal method. Briefly, $FeCl_3 \cdot 6H_2O$ (21.6 g) was dissolved in 320 mL EG, followed by the addition of NaAc (57.6 g) and PVA (6.4 g) under stirring (300 rpm). After 1 h, the mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 200 °C for 10 h. Then the prepared Fe_3O_4 nanoparticles were isolated from the solution with a magnet, washed by copious deionized water and dried at 60 °C for 8 h. The MNPs were then coated with silica to enhance their stability. (2) Bonding phenyl groups on Fe_3O_4–SiO_2. 3.5 g Fe_3O_4–SiO_2 from step 1 was put into 50 mL toluene containing 0.4 mL phenyltrichlorosilane under stirring. After 10 min, 0.4 mL pyridine was added into this stirred reactant, with refluxing for 8 h. The obtained product was washed carefully by MeOH and toluene several times, and then dried at 120 °C for 4 h. (3) Coating MC on Fe_3O_4–SiO_2–Ph. Three gram of Fe_3O_4–SiO_2–Ph from the step 2 was suspended in 100 mL of 0.2% (w/v) MC solution by sonication for 30 min under room temperature, followed by washing with water carefully and drying at 120 °C for 8 h.

2.5. MSPE procedure

The MSPE procedure was carried out as follows. The sample solution (1.5 mL) was adjusted to the desired NaCl concentration and pH, with the addition of the prescribed amount of Fe_3O_4–SiO_2–Ph–MC MNPs. The solution was sonicated for the prescribed time to extract analytes onto the MNPs. After extraction, an Nd–Fe–B magnet (50 mm × 50 mm × 10 mm) was attached to the vial bottom to isolate the MNPs from the suspension. After pouring the upper aqueous solution, 0.75 mL ultrapure water was added

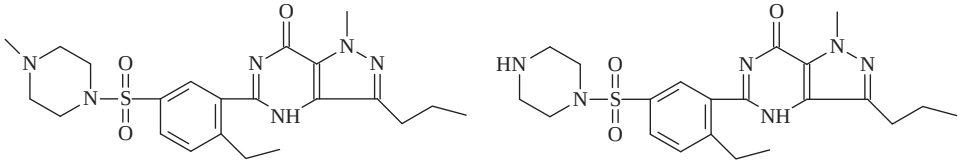

Fig. 1. The structure of SD and DD.

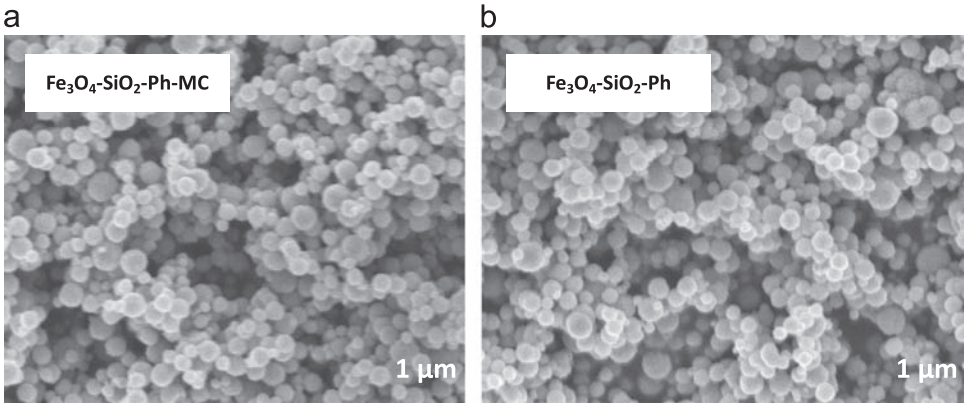

Fig. 2. SEM image of (a) Fe_3O_4–SiO_2–Ph–MC MNPs and (b) Fe_3O_4–SiO_2–Ph MNPs.

into the vial to wash the MNPs to remove the remnant sample solution. Desorption was preceded by adding a certain volume of eluant into the vial under ultrasonication for the certain time. After that, magnetic separation was performed and the eluate was collected for the HPLC analysis.

3. Results and discussion

3.1. Characterization of MNPs

To observe the morphology of the synthesized particles, Fe_3O_4–SiO_2–Ph and Fe_3O_4–SiO_2–Ph–MC MNPs were characterized by SEM. Obviously, from Fig. 2, both Fe_3O_4–SiO_2–Ph and Fe_3O_4–SiO_2–Ph–MC MNPs showed well-dispersed spherical morphology. The average diameter was estimated to be ~200 nm before and after MC coating, which demonstrated that MC was coated on MNPs in a form of film.

FT-IR characterization of Fe_3O_4–SiO_2–Ph, Fe_3O_4–SiO_2–Ph–MC and Fe_3O_4–SiO_2 MNPs were compared in Fig. 3. The absorption peaks around 1500 cm^{-1} were obvious for Fe_3O_4–SiO_2–Ph and Fe_3O_4–SiO_2–Ph–MC, but absent in the case of Fe_3O_4–SiO_2, which demonstrated that the phenyl groups were present in the first two materials. In addition, TGA was performed to evaluate the content of phenyl group and MC coating on MNPs. The weight loss ratios, ranging from 200 °C to 800 °C, were calculated to be 2.81% and 8.13% for Fe_3O_4–SiO_2–Ph and Fe_3O_4–SiO_2–Ph–MC MNPs, respectively. The data indicated that both phenyl group and MC coating were successfully modified on the surface of Fe_3O_4–SiO_2 MNPs.

To investigate the hydrophilicity of the material, the two MNPs before and after MC coating were dispersed in water. As shown in Fig. 4, the Fe_3O_4–SiO_2–Ph–MC MNPs dispersed well in water (Fig. 4a), while Fe_3O_4–SiO_2–Ph MNPs aggregated and floated over the water due to their strong hydrophobicity (Fig. 4b). This observation clearly demonstrated the better aqueous compatibility of Fe_3O_4–SiO_2–Ph–MC than Fe_3O_4–SiO_2–Ph, which would be a preferred merit for the following applications.

3.2. Optimization of MSPE conditions

The MSPE extraction was a complicated process which was controlled by multiple factors. In the present study, several influential factors, e.g. the amount of MNPs, sample pH, salt addition, extraction time, desorption solvent, volume of eluant and desorption time, were optimized in detail by a one-variant-at-one-time approach.

In our preliminary experiments, to ensure the complete elution of the target analytes from MNPs and the eluant compatible with the following HPLC system, the composition of the eluant was first

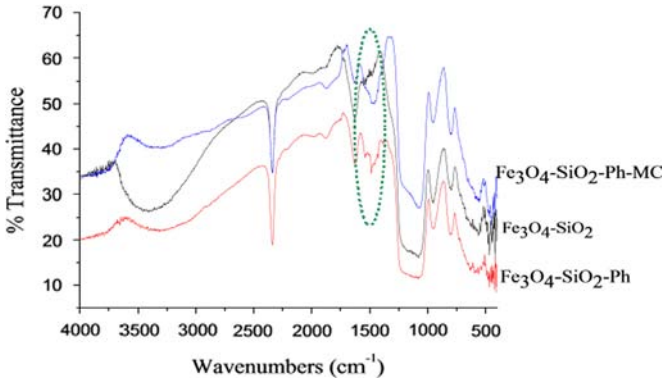

Fig. 3. The FTIR spectra of Fe_3O_4–SiO_2–Ph, Fe_3O_4–SiO_2 and Fe_3O_4–SiO_2–Ph–MC MNPs.

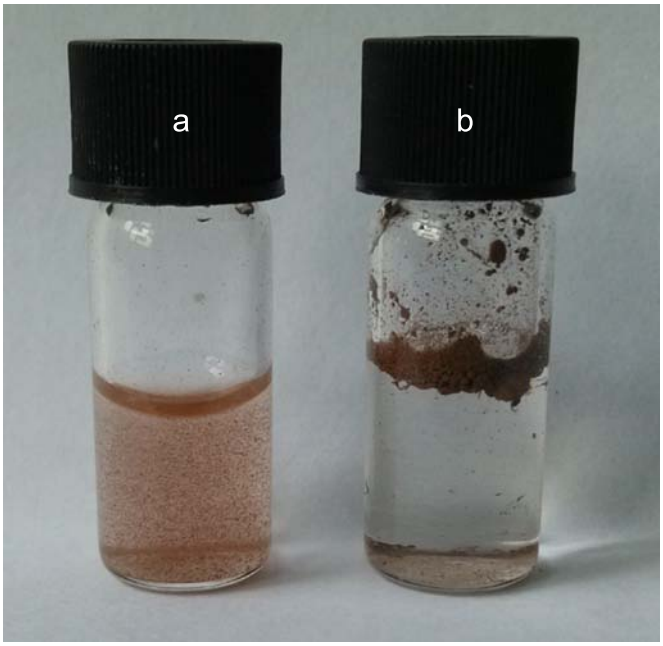

Fig. 4. Photographs of Fe_3O_4–SiO_2–Ph–MC MNPs (a) and Fe_3O_4–SiO_2–Ph MNPs (b) dispersed in water.

studied. A mixture of MeOH, water and HAc in a ratio of 75/25/1 (V/V/V) was chosen as it afforded the strongest analytical signals and symmetric HPLC peaks with high column efficiency.

The amount of the MNPs played a significant role for MSPE extraction capacity. It was studied in the range of 5–20 mg. Peak

areas of the two analytes decreased evidently with the increasing amount of MNPs from 5 to 20 mg, as shown in Fig. 5. The reason may be explained that the experiments of varied amount of MNPs were carried out with the fixed elution condition, i.e. 100 μL of the eluant, which may not be adequate to elute the adsorbed analytes effectively as the MNPs amount increased. Considering 5 mg of MNPs resulted in the highest analytical signals, it was chosen for the subsequent experiments.

The sample pH can affect the ionization status of the target analytes and influence the extraction performance further on. Hence, the effect of sample pHs in the range of 2.32–7.74 on the extraction was investigated. As shown in Fig. 6, the maximum peak area for DD occurred at the pH of 4.45, while the gradual enhanced peak area was observed for SD. The reason for the observation of sample pH influence could be as follows. At pH < 6.33, both SD (pKa = 6.03) and DD (pKa = 7.75) were positive charged and hydrophobicity of them was thus weakened.

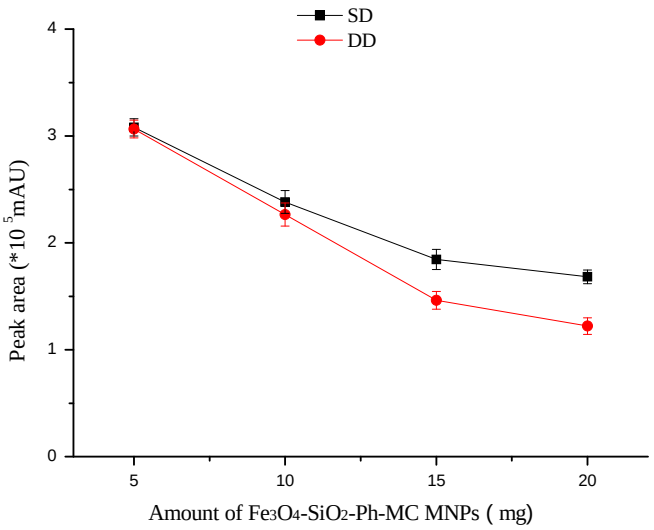

Fig. 5. Effect of the amount of Fe_3O_4–SiO_2–Ph–MC MNPs. Extraction condition: SD and DD concentration: 0.2 μg mL^{-1}; sample volume: 1.5 mL (pH = 6.33, unadjusted); salt concentration: 0 g mL^{-1}; extraction time: 10 min; eluant: mixture of MeOH, water and HAc in a ratio of 75/25/1(V/V/V); eluant volume: 100 μL; desorption time: 10 min.

As a result, interaction between them with phenyl groups was weak and low extraction efficiency was observed. With the increasing pH, protonation of SD and DD was decreased and hydrophobicity of them was increased; meanwhile, the residue silanol groups on MNPs ionized, which may have ion-exchange interaction with SD and DD. Hence, extraction efficiency of SD and DD was enhanced as a consequence of strengthened hydrophobic interaction and possible ion-exchange interaction. With the further increased pH to 7.74, although ion-exchange interaction between SD and silanol groups was weakened, hydrophobic interaction may be stronger, leading to similar extraction efficiency to that at the pH of 6.33; while hydrophobicity of DD ($\log P = 1.477 \pm 1.427$) was weaker than SD ($\log P = 2.468 \pm 1.427$), and decreased extraction efficiency was resulted. Therefore, sample pH was used without adjustment.

In our preliminary experiments, it was found that the MNPs tended to agglomerate in the sample solution in the presence of NaCl concentration ≥ 150 mg mL^{-1}. Therefore, the addition of NaCl to the sample solution was investigated in the range of 0–150 mg mL^{-1}. As seen from Fig. 7, it revealed that SD was very sensitive to the salt concentration with the abrupt decreasing of analytical signal once 10 mg mL^{-1} of NaCl was added in the sample solution; while, DD varied a little in the investigated salt concentration range. There were several reasons for these observations. Firstly, the addition of NaCl may favor the hydrophobic aggregation of MC on the surface of the material, leading to the poor dispersibility in the presence of high concentration of NaCl [29], as observed above. This was the negative factor for extraction efficiency. On the other hand, the addition of salt into the sample solution could influence the extraction performance positively or negatively as a result of salting-out or salting-in effect, respectively, or have no effect. Based on the observations in Fig. 7, salting-in effect may be predominant for SD as the analytical signals decreased abruptly in the presence of 10 mg mL^{-1} NaCl. However, DD ($\log P = 1.477 \pm 1.427$) was slightly more polar than SD ($\log P = 2.468 \pm 1.427$). Salting-out effect (increasing the extraction efficiency) may be obvious for relatively polar analytes [30]. Hence, the addition of the salt may facilitate the distribution of DD from the aqueous to MNPs. The above two factors contributed to the extraction efficiency of DD contrarily, and may compensate for each other, leading to the above observations. As no salt addition

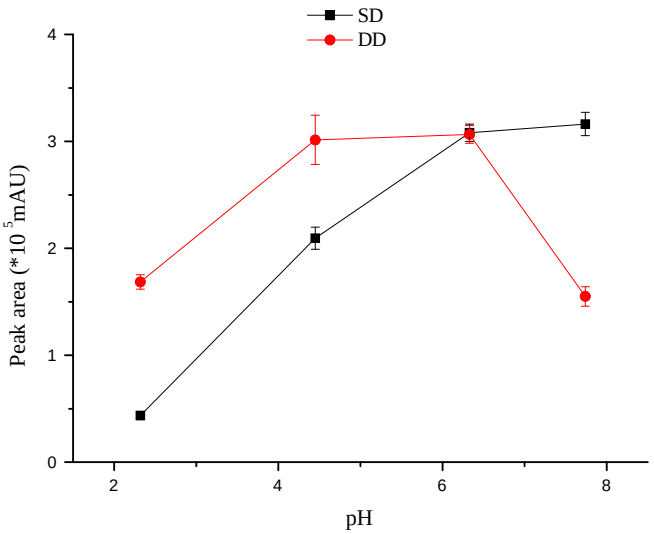

Fig. 6. Effect of sample pH. The amount of Fe_3O_4–SiO_2–Ph–MC MNPs: 5 mg; sample pH was adjusted in the range of 2.3–7.7. The other experimental conditions were the same as those in Fig. 5.

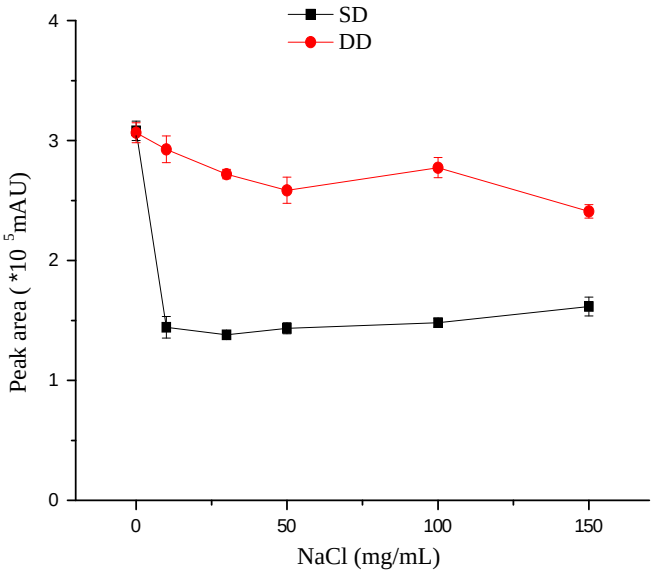

Fig. 7. Effect of salt addition in sample solution. The amount of Fe_3O_4–SiO_2–Ph–MC MNPs: 5 mg; NaCl concentration was adjusted in the range of 0–150 mg mL^{-1}. The other experimental conditions were the same as those in Fig. 5.

afforded the satisfactory extraction efficiency and the experimental operation was simple, this condition was chosen for the further investigations.

The influence of extraction time in the range of 5–20 min on the extraction efficiency was investigated and the results are depicted in Fig. 8. In the case of DD, the maximum peak area occurred at 10 min; while, the unilateral decreasing trend was observed for SD. It may be interpreted that the extraction was a dynamic process, and the adsorption of analytes might be slightly destroyed when the extraction time was prolonged [31]. As 10 min of extraction provided the satisfactory results for both the two analytes, it was chosen for the further experiments.

Desorption time is another significant factor influencing the extraction efficiency. When desorption time changed in the range of 5–20 min, the peak areas for two analytes varied a little (data not shown). This might be due to the strong elution ability of the eluant so that the analytes could be easily eluted from the sorbent in a short time. Hence, 5 min was selected for the following experiments in consideration of saving time. In addition, the volume of the eluant should be chosen based on the following considerations. It should be enough for repetitive injections (at least triple) for HPLC analysis, and to immerse the MNPs for effective desorption. Thus, the volume of eluant ranging from 80 to 150 μL was evaluated, and the peak areas decreased dramatically with the increasing eluant volume from 80 to 150 μL. Therefore, 80 μL of eluant was the optimal condition.

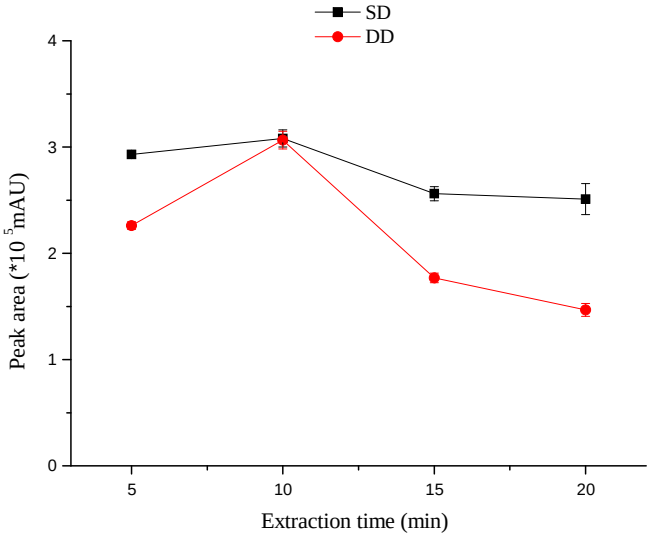

Fig. 8. Effect of extraction time. The amount of Fe_3O_4–SiO_2–Ph–MC MNPs: 5 mg; the extraction time was in the range of 5–20 min. The other experimental conditions were the same as those in Fig. 5.

In summary, the optimal extraction conditions for MSPE of SD and DD were 5 mg of MNPs, 1.5 mL of sample solution with no salt addition and unadjusted pH (≈ 6.33), and extraction time of 10 min. The optimized elution solvent was a mixture of MeOH, water and HAc in a ratio of 75/25/1(V/V/V) and desorption time was 5 min.

3.3. Method evaluation

To evaluate the proposed method, the ultrapure water samples were spiked at eight concentration levels of target analytes from 2.5 to 400 ng mL^{-1}, followed by MSPE under the above optimized conditions and HPLC analysis. Linearity ranges were calculated by plotting corresponding HPLC peak areas (y) versus concentrations of analytes (x, ng mL^{-1}). The results are presented in Table 1. The linearity ranges of SD and DD were 5–400 ng mL^{-1} (r^2=0.9968) and 2.5–400 ng mL^{-1} (r^2=0.9983), respectively. Intra-day and inter-day precision were both evaluated at three concentration levels and each concentration level was repeated three times. The intra-day and inter-day relative standard deviations (RSDs) were in an acceptable range of 1.7%–11.8%, which proved that the proposed method was endowed with acceptable reproducibility. Limits of detection (LODs) were as low as 0.58 ng mL^{-1} (SD) and 0.64 ng mL^{-1} (DD), respectively, which were calculated at a signal-to-noise ratio of 3. All these data demonstrated that the proposed method was reliable.

3.4. Method applications to biological samples

Under the optimized conditions, the proposed method was applied to determinate the two target analytes in human plasma and urine. Even though these samples are complex, no extra pretreatment before MSPE was required. Blank blood and urine samples were subjected to the extraction process under the optimum conditions, and no obvious interference peaks were found. Spiked real samples were then subjected to the extraction and results are shown in Table 1. For human plasma samples, SD and DD had good linearity ranges of 5–200 (r^2=0.9972) and 5–400 ng mL^{-1} (r^2=0.9956), respectively. The RSDs of intra-day and inter-day (n=3) for two analytes were in the range of 2.6–8.2%. LODs for SD and DD were 0.68 ng mL^{-1} and 0.96 ng mL^{-1}, respectively.

For urine samples, as shown in Table 1, the linearity ranges of SD and DD were 5–200 (r^2=0.9972) and 5–400 ng mL^{-1} (r^2=0.9959), respectively. The RSDs of intra-day and inter-day (n=3) ranged from 0.6% to 7.2%. The LODs were 0.41 ng mL^{-1} and 0.80 ng mL^{-1} for SD and DD, respectively.

Chromatograms obtained from the extraction of spiked water and biological sample are shown in Fig. 9.

Table 1
Regression data and LODs of SD and DD extracted with Fe_3O_4–SiO_2–Ph–MC MNPs in various samples.

Samples	Analytes	Linearity range (ng mL^{-1})	r^2	LOD (ng mL^{-1})	Intra-day RSD (%, n=3)			Inter-day RSD (%, n=3)		
					10 ng mL^{-1}	50 ng mL^{-1}	200 ng mL^{-1}	10 ng mL^{-1}	50 ng mL^{-1}	200 ng mL^{-1}
Water	SD	5.0–400	0.9968	0.58	8.9	8.5	6.4	6.1	11.8	1.7
	DD	2.5–400	0.9983	0.64	8.8	6.5	11.6	3.6	7.1	5.3
Plasma	SD	5.0–200	0.9972	0.68	4.2	3.7	2.9	3.9	3.9	7.9
	DD	5.0–400	0.9956	0.96	7.3	8.2	3.0	2.6	4.4	7.5
Urine	SD	5.0–200	0.9972	0.41	2.8	2.9	0.6	2.9	6.1	3.5
	DD	5.0–400	0.9959	0.80	7.2	3.6	2.4	2.3	5.7	7.0

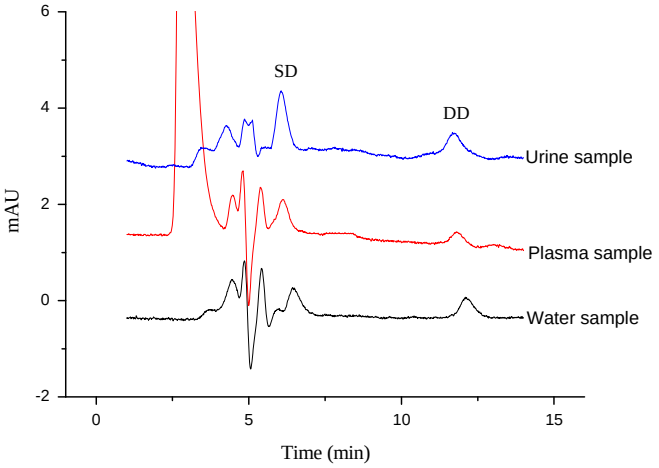

Fig. 9. Chromatograms of spiked water and biological sample at the concentration level of 10 ng mL^{-1}.

SPE based on commercial Bond Elut LRC Certify and molecularly imprinted polymers were reported to extract SD and DD from biological samples followed by GC–MS and HPLC-UV analysis [32,33]. Compared to these two studies, the proposed method showed comparable linearity ranges with better r^2 and lower LODs, which indicated that it was promising for SD and DD determination.

4. Conclusion

In this work, Fe_3O_4–SiO_2–Ph–MC sorbent was successfully prepared for the extraction of sildenafil and its metabolite, desmethyl sildenafil, in water and biological samples. The coating of methylcellulose endued the MNPs with excellent dispersibility in aqueous solution and thus enhanced the extraction efficiency. The material exhibited good performance on blood and urine samples with acceptable recovery, satisfactory reproducibility and low limits of detection. It has great potential in the preconcentration of trace analytes in complex matrix.

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