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ORIGINAL PAPER

Efficient dispersive micro solid-phase extraction of antidepressant drugs by a robust molybdenum-based coordination polymer

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Abstract

A molybdenum-based coordination polymer $\{[Mo(PDA)(NO)(\mu\text{-}O)MoO_3]\cdot 1.42H_2O\cdot 0.58C_2H_5OH\}_n$ (**1**) (PDA is 1,10-phenanthroline-2,9-dicarboxylate) was synthesized using solvothermal reaction conditions and characterized using a suite of analytical techniques. Single-crystal X-ray diffraction studies reveal a 1D chain structure, with close contacts expanding the structure into 3D including π-interactions and hydrogen bonding. The utility of **1** as a sorbent for dispersive micro solid-phase extraction (D-μSPE) of basic organic compounds such as antidepressants is supported by the presence of many functional groups on the surface of **1** (such as pendant carboxylates, Mo=O, Mo–NO, and CH groups) as well as extensive electrostatic interactions. Therefore, **1** can be a suitable choice as sorbent in the D-μSPE of antidepressant drugs from human plasma samples via appreciable adsorbate-adsorbent interactions. Determination of the extracted antidepressant drugs was conducted using high-performance liquid chromatography-ultraviolet (HPLC-UV), with calibration plots being linear in the concentration range 0.1–500 ng mL^{-1} for amitriptyline and nortriptyline, 0.2–500 ng mL^{-1} for imipramine, and 0.5–300 ng mL^{-1} for sertraline. The relative standard deviation (RSD) values were calculated for both intra-day and inter-day precision, and the RSD% values were in the range 3.9 to 5.2% and 4.6–5.4%, respectively. The limits of detection (LODs) was determined as 0.03–0.2 ng mL^{-1}. Due to the good stability and reusability of the sorbent, the adsorption capacity had no obvious decrease after being used 20 times. Finally, the D-μSPE-HPLC-UV method was applied for the determination of antidepressant drugs in human plasma samples with recoveries of the analytes in the range 94.9 to 102%.

Keywords Coordination polymer · Powder X-ray diffraction · Adsorbate-adsorbent interactions · HPLC · Plasma analysis

Introduction

Selective serotonin reuptake inhibitors (SSRI) and tricyclic antidepressants (TCAs) are primarily used in the therapy of depression and other mental disorders [1, 2]. The chemical analysis of these compounds and metabolites thereof in biological samples is, therefore, an important aspect of therapeutic drug monitoring and toxicology [3]. Due to the complexity of biological matrices and low analyte content (below the detection limit of the analytical instrument), sample preparation before analysis is required [4, 5].

Until recently, various extraction methods such as solid-phase extraction (SPE) [6], solid-phase microextraction (SPME) [7], effervescent-assisted dispersive magnetic micro solid-phase extraction (EA-DM-μSPE) [8], magnetic solid-phase extraction (MSPE) [9], dispersive liquid-liquid microextraction (DLLME) [8], and hollow-fiber liquid-phase microextraction (HF-LPME) [9] have been used for the extraction of antidepressants from biological fluids. The development of dispersive micro solid-phase extraction (D-μSPE) facilitates the extraction of target analytes from solution by dispersion of the sorbent in the sample solution. The principle of D-μSPE is based upon the existence of strong interactions between target analytes and the sorbent material. Where this occurs, the extraction method exhibits advantages such as

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simplicity, speed, and efficiency over other more traditional extraction methods [10–12]. The discovery of novel sorbents that display specificity for analytes is, therefore, an important criterion regarding the implementation of the method in the analysis of relevant compounds. Due to the poor recoveries or unrecyclable processes of many sorbents used in the D-μSPE method, choosing a robust, high-capacity sorbent remains a challenge. Recently, water-stable CPs/MOFs have been widely used as sorbents in many sorption-related fields [13].

Over the past decade, the class of materials referred to as either coordination polymers (CPs) or metal-organic frameworks (MOFs) has been extensively investigated as new types of sorbent materials for various pretreatment methods. Reasons for this include numerous examples with excellent thermal and chemical stability, diverse structural topologies and compositions, tunable surface area, and porosity [14–22].

The adsorption mechanism in CPs/MOFs can be attributed to one or both of the following: (i) host-guest interactions between analytes and pores of the sorbents and (ii) possible formation of electrostatic interactions between the analytes and sorbents like hydrogen bonding, π-interactions or multiple, and weak (e.g., van der Waals or dispersion) interactions. An important example is the investigation of MIL-101(Fe) and amino-functionalized MIL-101(Fe) in the extraction of the bisphenol family (BP) of compounds by the dispersive solid-phase extraction (DSPE) method. Although the sorbent ability of both these MOFs benefits from their high surface area, large pore size, and π-interactions, NH_2-MIL-101(Fe) demonstrated better results for the preconcentration and determination of trace-level BPs. This can be attributed to hydrogen bonding between the N-H group of this MOF and the OH group of target analytes [23]. Therefore, the purposeful selection of organic ligands in the construction of new sorbents can highly affect the final adsorption results [24, 25].

It is important to note that washing off /eluting the extracted analytes with solvents is a crucial step in the D-μSPE method. Therefore, moisture (solvent)-sensitive CPs/MOFs cannot be reused after elution. For example, MOF-5 with high surface area (with 2900–3400 $m^2\ g^{-1}$) and high thermal stability (up to 400 °C) seems to be a good sorbent; however, its water-sensitive nature is its biggest drawback (its structure collapses after exposing to the ambient atmosphere for 10 min) [26]. Therefore, designing and synthesizing robust sorbents can be a hot research topic. It is important to note that the molybdenum-based CPs/MOFs have not been much considered in the past due to their complicated reaction conditions [27] which will be further considered by the CSD (Cambridge Structural Database) survey in the Electronic Supplementary Material (ESM). However, this high-valent metal ion tends to have strong coordination bonds to the carboxylate ligands (due to the hard/soft acid-base principle) and makes stable structures. Also, molybdenum-containing frameworks are currently used in a wide range of applications and are therefore of general scientific interest across numerous fields of research including catalysis, sorption, electrical conductivity, and optical materials [28–33].

We report here the solvothermal synthesis of a robust molybdenum-based coordination polymer $\{[Mo(PDA)(NO)(\mu\text{-}O)MoO_3]\cdot 1.42H_2O\cdot 0.58C_2H_5OH\}_n$ (**1**) with significant thermal/moisture/chemical stability and the presence of functional groups in the structure making it suitable for use as a sorbent for the D-μSPE of antidepressant drugs (i.e. amitriptyline, nortriptyline, imipramine, and sertraline) from human plasma followed by high-performance liquid chromatography with ultraviolet detection (HPLC-UV).

Experimental

Chemicals and materials

All reagent chemicals were commercially purchased from Merck (Darmstadt, Germany, www.merckmillipore.com) and used without further purification except for 1,10-phenanthroline-2,9-dicarboxaldehyde (H_2ALD), which was synthesized according to a literature method [34]. Amitriptyline (99%), nortriptyline (98%), imipramine (99%), and sertraline (98%) were obtained from Sigma-Aldrich (St. Louis, MO, USA, www.sigmaaldrich.com). The molecular structure and chemical properties of the model drugs are shown in Table S1.

Preparation of standard solution and real samples

A stock solution of 10 mg L^{-1} of analytes was prepared in HPLC-grade methanol and stored at 4 °C. The working standard solutions were prepared by subsequent dilutions. The blank human plasma samples were collected from healthy volunteers and stored at − 18 °C. No medications were administered to healthy volunteers before the experiments. The blank human plasma samples were used for both optimization and validation of the D-μSPE method. Different amounts of antidepressant drugs were spiked into the plasma samples, and the resulting solutions were subjected to the following D-μSPE procedure. Also, the plasma samples from three depressed female patients treated with antidepressant drugs were obtained. The collected blood samples were centrifuged at 1000*g* for 10 min to remove cells from the samples. Then, to remove blood platelets and proteins, the plasma samples were mixed with acetonitrile and centrifuged for 15 min at 2000 g. Finally, the plasma samples were stored at − 18 °C.

Instrumentation

Chromatographic separations were performed with a Knauer HPLC instrument equipped with a UV detector and manual sample injector fitted with a 20 μL injection loop (*Knauer* Company, Berlin, Germany, www.knauer.net). The target analytes were separated by the ODS3 column (4.6 mm ID × 250 mm length, 5 μm particle diameters). The mobile phase at a flow rate of 1.0 mL min^{-1} was a mixture of 0.05 M phosphate buffer (pH 4.0) and acetonitrile (40:60 v/v) with isocratic elution. The wavelength of the UV detector was set at 210 nm. The infrared spectra were recorded in the range of 4000–400 cm^{-1} on a Thermo Nicolet/AVATAR 370 Fourier transform spectrophotometer (www.thermofisher.com) using KBr discs. Elemental analysis (CHN) was performed using a Thermo Finnigan Flash EA 1112 microanalyzer. Thermal gravimetric analysis (TGA) was carried out under an air atmosphere from ambient temperature up to 950 °C with a heating rate of 10 °C min^{-1} on a Shimadzu TGA-50 instrument (www.shimadzu.com). A summary of the crystallographic data and the structure refinements are provided in Table S3. Powder X-ray diffraction (PXRD) data were collected on ASENWARE/AW-XDM300 X-ray powder diffractometer using Cu Kα (λ = 1.54184 Å) radiation at room temperature with the scan range 2θ = 5 to 50° and step size of 0.05° and step time of 1 s. X'Pert HighScore Plus was used to compare the experimental PXRD pattern with the simulated lines from the crystal structure. Room-temperature UV-Vis diffuse reflectance (DR UV-Vis) spectra were collected on a finely ground sample with a Scinco S400 spectrophotometer (www.scinco.com), and diffuse reflectivity was measured from 200 to 1000 nm. Adsorption studies were performed using a BELSORP Mini II surface area analyzer from Micromeritics Instrument Corporation with N_2 at 77 K (www.microtrac.com). The field emission scanning electron microscope (FESEM) analysis was conducted on MIRA3 TESCAN (Tescan Co., Czech Republic, www.tescan.com).

Synthesis of (1) $\{[Mo(PDA)(NO)(\mu\text{-}O)MoO_3]\cdot 1.42H_2O\cdot 0.58C_2H_5OH\}_n$

An aqueous solution of sodium borohydride (3 mL) (1 mg, 0.24 mmol) was added to an ethanolic solution of H_2ALD (10 mL) (30 mg, 0.12 mmol), and the mixture was stirred at 60 °C for 30 min. Then, an aqueous solution of $Ce(NO_3)_3\cdot 6H_2O$ (3 mL) (54 mg, 0.12 mmol) was added and the dark red solution was stirred for a further 30 min (local pH = 6.2). Afterwards an aqueous solution of $H_3PMo_{12}O_{40}$ (PMo_{12}) (3 mL) (90 mg, 0.05 mmol) was added and the dark green solution was stirred for an extra hour at 60 °C (local pH = 2.3). The mixture was sealed in a 30-mL Teflon-lined reactor and heated at 130 °C for 72 h and then cooled to room temperature at a rate of 10 °C h^{-1}. Orange cubic-like crystals of the **1** were obtained in 70% yield (based on Mo). Anal. Calcd. For $C_{15.15}H_{12.32}Mo_2N_3O_{11}$ (%): C, 30.11; H, 2.06; N, 6.95; Mo, 13.87; Found: C, 28.06; H, 1.71; N, 7.16; Mo, 14.26. FTIR (KBr pellet, cm^{-1}): 3441, 3288, 3092, 3068, 1696, 1660, 1608, 1512, 1467, 1418, 1348, 1312, 1268, 1170, 1130, 959, 874, 822, 762, 698, 604, 575, 480, 436 (Fig. S1).

Extraction procedure

The D-μSPE procedure was carried out as follows: first, 10 mg of **1** was added to 5 mL of the sample solution (pH 5.0) containing the target drug analyte. Subsequently, the solution was ultrasonicated for 2 min to ensure sufficient contact between the analytes and the sorbent. After extraction, the sorbent was collected by centrifugation for 5 min at 3075 g, and the supernatant was discarded. Before the desorption of the analytes, the sorbent was dried with a current of nitrogen gas. The extracted analytes were eluted with 300 μL acetonitrile/ammonia (80/20 v/v) solvent ultrasonically for 1 min and centrifuged at 3075*g* for another 5 min. Then, the eluent was evaporated and dried under a gentle stream of nitrogen gas at room temperature, and the sediment phase was dissolved in 50 μL of acetonitrile. The time required to carry out the whole sample preparation procedure is 17 min. Finally, for the analysis, 20 μL of the solution was injected into the HPLC-UV system.

X-ray crystallographic analysis

Single-crystal X-ray diffraction data, data collection, and structure refinement details are summarized in Table S3. Diffraction data of **1** are collected on an Agilent SuperNova single-crystal X-ray diffractometer with graphite-monochromated Cu Kα radiation (λ ~ 1.54 Å) at 130 K (Table S3). The structure was solved by direct methods using the program SHELXS and refined by full-matrix least-squares methods on F^2 using SHELXL. A multi-scan absorption correction was applied. Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number 2009401.

Results and discussion

Characterization of materials

PXRD analysis

It is well known that moisture stability is a crucial property for any material to be used industrially since water is abundant in the preparation, storage, transportation, and application processes. To check this, the crystals of **1** are immersed in water

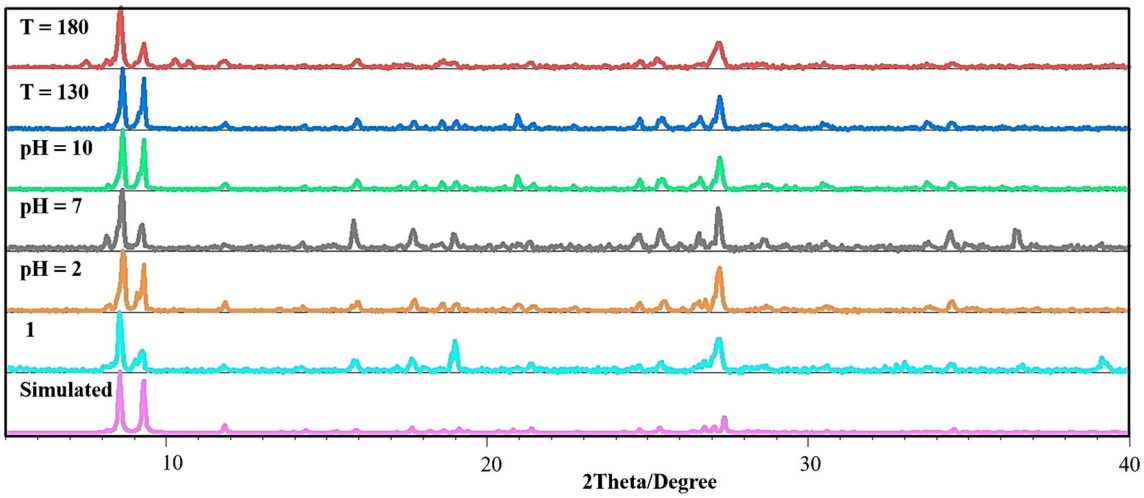

Fig. 1 Comparison of PXRD patterns of **1** (with the simulation generated by mercury) at different pH and temperatures

for 7 days, and PXRD analyses show little change in the powder pattern as compared with that of pure **1** indicating its high chemical stability toward moisture (Fig. 1). Also, **1** was soaked in aqueous media over a wide pH range of 2.0 to 10.0 for 24 h at ambient conditions. PXRD analyses show that **1** preserves its crystallinity under these conditions as well (Fig. 1). Interestingly, **1** is also stable under vacuum at 130 and 180 °C for 12 h (Fig. 1). Therefore, the result of this analysis showed that **1** can be survived under harsh conditions due to its unique and robust structure.

Single-crystal X-ray diffraction analysis

The synthesis of **1** is summarized in the Supplementary Material (ESM). Also, the infrared and ultraviolet-visible spectra as well as the thermogravimetric analysis are consistent with the single-crystal X-ray diffraction data of **1** (ESM). As can be seen in the structure of **1**, there are many pendant carboxylates, Mo = O, Mo–NO, and CH functional groups as well as extended electrostatic interactions such as π-interactions and hydrogen bonds. So, all these features, together with the structural stability of **1** under harsh conditions, make it a good candidate as a sorbent for antidepressant drugs since antidepressants contain some functional groups like NH, CH, Cl, and unsaturated rings which can electrostatically interact with **1**.

Field emission scanning electron microscope analysis

Fig. 2 shows the surface morphology of the sorbent using FESEM images which showed the rough surface.

Optimization of the D-μSPE conditions

To achieve greater extraction efficiency, the optimization of the experimental parameters is necessary. All the experiments were performed in triplicate, and the means of the results were used for optimization. Here, the effect of some parameters including sorbent amount (4–20 mg), sample pH (2.0–10.0), elution solvent, acetonitrile/ammonia (80/20 *v*/v) (100–500 μL), elution time (0.5–2 min), and extraction time (0.5–4 min) was investigated and optimized. Respective data and figures are given in the ESM (Figs. S10–S14). The following experimental conditions were found to give best results: (a) sorbent amount, 10 mg; (b) sample pH, 5; (c) elution solvent: acetonitrile/ammonia (80/20 v/v); (d) acetonitrile/ammonia (80/20 v/v), 300 μL; (e) elution time, 1 min; and (f) extraction time, 2 min.

Method validation

The analytical performance of the D-μSPE-HPLC-UV method including linear range, limits of detection (LODs), extraction recovery (ER), and precision is evaluated (Table S7). The linearity of the D-μSPE-HPLC-UV method was determined with drug-free human plasma samples spiked with the analytical standards of antidepressants. The calibration plots are linear in the range of 0.1–500 ng mL^{-1} for amitriptyline, and nortriptyline, 0.2–500 ng mL^{-1} for imipramine, 0.5–300 ng mL^{-1} for sertraline (Fig. S15). The correlation coefficients ranged from 0.9935 to 0.9987. The LOD of the method was calculated as the concentration corresponding to three times the signal-to-noise ratio and was in the range of 0.03 to 0.2 ng mL^{-1}. The intra-day precision was studied based on three successive extractions at

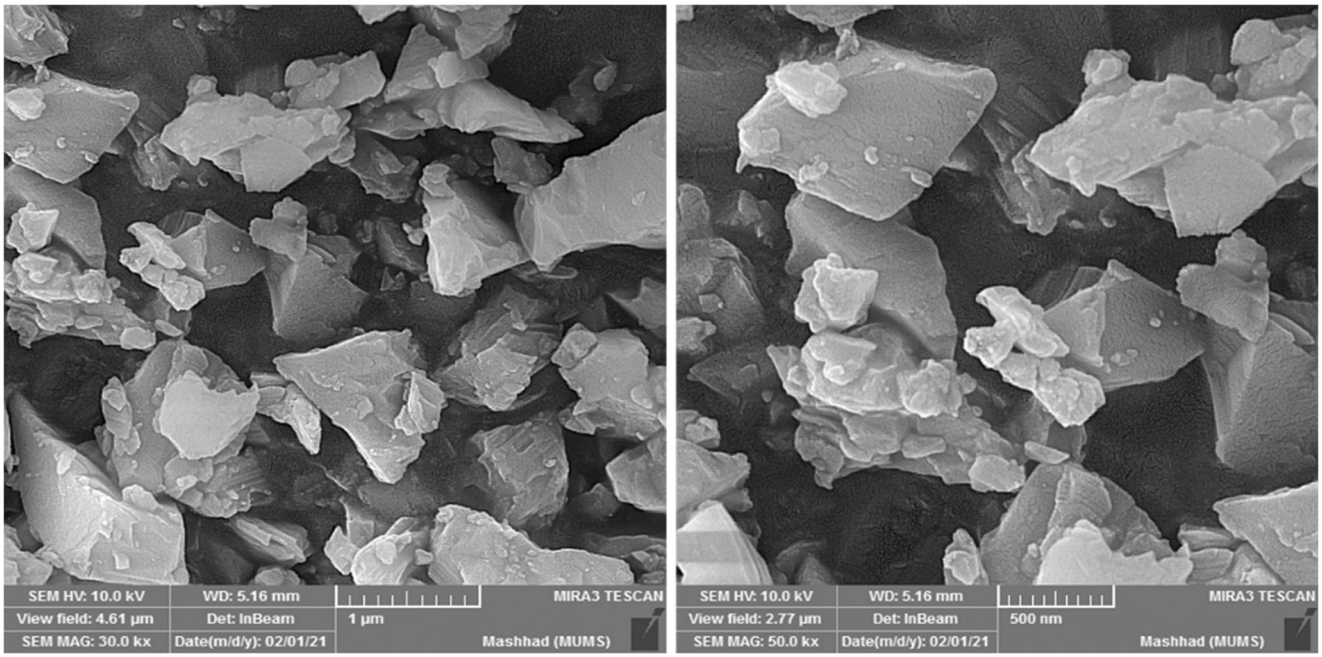

Fig. 2 FESEM images of **1**

different concentration levels (0.5, 5, and 200 ng mL^{-1}). The inter-day precision was determined over 3 days spiked at 0.5 ng mL^{-1}. The relative standard deviations (RSDs) for intra-day precision and inter-day precision varied from 3.9 to 5.2% and 4.6 to 5.4%, respectively. The ER% was defined as the percentage of total analyte moles (n_0) extracted to the extracted phase (n_f):

$$ER\% = \frac{n_f}{n_0} \times 100 = \frac{C_f}{C_0} \times \frac{V_f}{V_s} \times 100$$

where V_f and V_s are the eluent volume and sample volume, respectively. The absolute extraction recoveries were in the range 88.9–92.6%.

Reusability (adsorption-desorption cycles) of **1** was investigated for the determination of its shelf life. Calculating the extraction efficiency after at least 20 usages indicates that it is still stable and reusable (Fig. S16). Also, Fig. S17 shows the XRD patterns of the sorbent before and after 20-time usages. The results showed that the sorbent has good chemical/mechanical stability without any significant loss of the adsorption capacity.

Table 1 The results of plasma samples from depressed patients with the D-μSPE-HPLC-UV method

Sample	Analyte	Concentration (ng mL^{-1})	Relative recovery (%)		RSD (%) at 0.5 (ng mL^{-1})
			0.5 (ng mL^{-1})	50 (ng mL^{-1})	
Patient 1	Amitriptyline	38.0	95.7	96.3	5.7
	Nortriptyline	ND	96.6	97.8	6.0
	Imipramine	ND	94.9	96.1	5.3
	Sertraline	ND	96.9	97.7	5.2
Patient 2	Amitriptyline	ND	98.7	100	5.8
	Nortriptyline	56.9	98.9	99.6	5.9
	Imipramine	ND	97.5	98.1	5.4
	Sertraline	ND	98.6	98.9	6.2
Patient 3	Amitriptyline	ND	97.9	99.2	5.4
	Nortriptyline	ND	100	101	5.3
	Imipramine	ND	96.5	98.6	5.7
	Sertraline	5.0	99.6	102	5.8

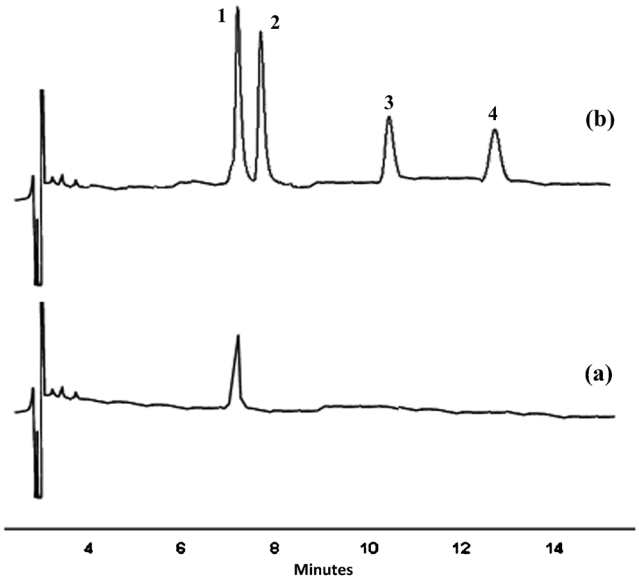

Fig. 3 HPLC–UV chromatograms of (**a**) non-spiked and (**b**) spiked human plasma samples at 50 ng mL^{-1}. Peak numbers correspond to (1) amitriptyline, (2) imipramine, (3) nortriptyline, and (4) sertraline

Analysis of real samples

To evaluate the efficiency of the D-μSPE-HPLC-UV method, it was applied to the analysis of plasma samples from three depressed female patients treated with antidepressant drugs. Patient 1 (age 33) was treated with amitriptyline (25 mg, twice a day), patient 2 (age 35) was treated with nortriptyline (25 mg, twice a day), and patient 3 (age 36) was treated with sertraline (50 mg, once a day). The results are summarized in Table 1. Also, the accuracy of the method was evaluated, and relative recovery studies were done with real samples spiked at different concentration levels (0.5 and 50 ng mL^{-1}). The results (Table 1) show that the relative recoveries of the antidepressant drugs ($n = 5$) were obtained between 94.9 and 102% and RSDs ranging from 5.2 to 6.2%. Fig. 3 illustrates the HPLC-UV chromatograms of the human plasma sample from the depressed patient under treatment with amitriptyline (a) before and (b) after spiking with antidepressant mixture standard solution at a concentration level of 50 ng mL^{-1}. Peak shapes and resolution indicated that the D-μSPE-HPLC-UV method are not any noteworthy impact of the sample matrix on the analytical performance of the method.

Comparison of the proposed method with previously reported results

The D-μSPE-HPLC-UV method was compared with the previously reported methods for the determination of antidepressant drugs. As shown in Table 2, the D-μSPE-HPLC-UV method exhibits several advantages over previously reported methods [35–40]. The LODs of the current method were less than other previous methods. Also, the D-μSPE-HPLC-UV method exhibited a wide linearity range, and desirable precision, which were superior to or comparable with other listed methods. The total sample preparation time of the D-μSPE-HPLC-UV method is obtained 17 min that is shorter than the extraction time of FPSE-HPLC-DAD (30 min) [37], and HF-LPME-LC-UV (45 min) [39], comparable with in-tube SPME-HPLC-UV (16 min) [17], and higher than EA-DM-μSPE-HPLC-UV (6 min) [8], MSPE-GC-MS (6 min) [9], DLLME-GC-MS (11 min) [36], and MSPE-HPLC-UV (5 min) [40]. Certainly, magnetizing the sorbent can reduce the extraction time of the D-μSPE-HPLC-UV method.

Table 2 Comparison of the D-μSPE-HPLC-UV method with other related methods for the determination of antidepressant drugs

Method	Sample	Detection system	LOD (ng mL^{-1})	Linear range (ng mL^{-1})	Total sample preparation time (min)	RSD (%)	Ref.
EA-DM-μSPE	Urine, pharmaceutical wastewater	HPLC-UV	0.03–0.05	0.07–2000	6	1.1–2.0	[8]
MSPE	Urine, plasma, water	GC-MS	0.008–0.028	0.05–500	6	4.1–9.9	[9]
DLLME	Urine	GC-MS	1.0–2.0	2–100	11	4.0–9.9	[35]
FPSE	Urine	HPLC-DAD	150	500–20,000	30	2.3–13.9	[36]
PMME	Urine	HPLC-UV	0.7–1.4	5–1000	–	0.4–10.1	[37]
HF-LPME	Urine, plasma, water	LC-UV	0.5–0.7	5–500	45	2.0–12.0	[38]
MSPE	Plasma, water	HPLC-UV	2–4	5–800	5	3.5–4.6	[39]
In-tube SPME	Plasma	HPLC-UV	40	80–1000	16	1.1–3.5	[40]
D-μSPE	Plasma	HPLC-UV	0.03–0.05	0.1–200	17	4.1–6.6	This study

DLLME, dispersive liquid-liquid microextraction; *EA-DM-μSPE*, effervescent-assisted dispersive magnetic micro solid-phase extraction; *FPSE*, fabric phase sorptive extraction; *PMME*, polymer monolith microextraction; *HF-LPME*, hollow-fiber liquid-phase microextraction; *MSPE*, magnetic solid-phase extraction; *SPME*, solid-phase microextraction

Concluding remarks

In this work, **1** is one of the few examples of molybdenum-based coordination polymers that are synthesized by solvothermal methods. It was the entirely unexpected but repeatable product obtained from planned reaction and has a robust structure. Although non-covalent intermolecular interactions such as π-interactions and hydrogen bond are not only considered to increase the dimensions of **1**, they also enhance its stability. **1** shows the unique properties that make its potential applications as an adsorbent for effective D-μSPE of antidepressant drugs in plasma samples. The method is fast and sensitive, has a low RSD, a wide linear range, much shorter extraction time, and insignificant matrix effect for antidepressant drugs. Remarkably, this sorbent material is highly washable and reusable as the adsorbed analytes could be easily washed off by common organic solvents and demonstrated excellent recovery and reusability after 20-time usages.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00604-021-04767-4.

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Declarations

Conflict of interest The authors declare no competing interests.

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