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Review Article

Sorbent based extraction for pre-concentration of antidepressant drugs: A review

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Abstract
The detection and quantification of antidepressant drugs in biological and environmental samples are crucial for therapeutic drug monitoring, forensic analysis, and environmental safety. Sorbent-based extraction techniques have emerged as effective methods for the pre-concentration of these drugs, offering advantages such as high sensitivity, minimal solvent consumption, and improved selectivity. Over the decade (2015 to 2025), 92 publications have documented progress in the development and application of sorbent materials for the detection and quantification of antidepressants in various environmental and biological matrices. This review provides a comprehensive overview of various sorbent materials, including carbon-based, polymeric, and magnetic sorbents, emphasizing their extraction mechanisms, efficiency, and compatibility with different analytical techniques. Additionally, the integration of novel nanomaterials and functionalized sorbents has significantly enhanced extraction performance, enabling better analyte recovery and lower detection limits. The article also discusses recent advancements, optimization strategies, and the potential of sorbent-based techniques in pharmaceutical and environmental applications. Finally, current challenges, including sorbent stability, reusability, and matrix effects, are examined, along with future perspectives to further improve the efficiency and sustainability of these extraction methods.

Keywords: emerging contaminant, functionalise materials, microextraction, psychoactive drugs, solid-phase extraction

Introduction

Depression is a leading mental health disorder worldwide and cause of global disease burden, recognized as a severe and often chronic illness. Symptoms of depression include mood disturbances, persistent fatigue, sleep disruptions, loss of interest and motivation, impaired social and occupational functioning, and, in severe cases, suicidal thoughts or behaviours [1-3]. Treatment typically involves psychotherapy or pharmacotherapy, primarily using antidepressant drugs. Clinically, depression is diagnosed based on the presence of abnormal positive affect (anhedonia) and negative affect (low mood, feelings of helplessness, coping deficits, and fatigue). Physiological abnormalities associated with depression include hyperactivity of the hypothalamic–pituitary–adrenal (HPA) axis and dysregulation of the autonomic nervous system [4,5]. Historically, tricyclic antidepressants (TCAs) were the primary pharmacological treatment for depression; however, their use has declined due to significant cardiovascular side effects and the risk of overdose. Currently, second-generation antidepressants drugs, such as selective serotonin reuptake inhibitors (SSRIs), serotonin and norepinephrine reuptake inhibitors (SNRIs), and noradrenergic and specific serotonergic antidepressants (NaSSAs), are more commonly prescribed. These medications primarily target serotonin and norepinephrine neurotransmission to alleviate depressive symptoms [6, 7].

In pharmaceutical formulations, the active pharmaceutical ingredient (API) is a main substrate, and following drug administration, its analysis in complex matrices such as biological fluids or environmental samples is essential for both therapeutic drug monitoring and the detection of excreted metabolites. Antidepressant measurement in biofluids ensures drug quality, optimal therapy, and minimal overdose risk [8, 9]. However, these analyses often present challenges due to the complexity of the

sample matrix and the low concentration of target compounds, frequently falling below the detection limits of chromatographic systems. To address these limitations, the application of good sample separation and enrichment techniques utilizing an appropriate carrier system is preferred [10-13].

Conventional approaches such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE) have been widely employed for this purpose. SPE is recognized for its efficient sample clean-up, and its final extracts are typically well-suited for various analytical techniques. Similarly, LLE is a relatively simple and cost-effective method that provides effective sample purification, particularly for plasma samples. However, achieving high analyte enrichment with LLE is often challenging due to limitations in sample volume and material availability. Formation of emulsion is a major drawback during LLE process [14, 15]. Despite their widespread application, LLE present notable drawbacks, including labour-intensive procedures, time-consuming workflows, and a high dependency on organic solvents, raising concerns regarding environmental sustainability. Additionally, these methods are predominantly manual, further limiting their efficiency in high-throughput analyses.

Among the various techniques available for sample preparation, sorbent-based extraction methods have gained significant attention due to their ability to selectively isolate and concentrate target analytes from complex sample matrices. These methods rely on the interactions between the analytes and specially designed sorbent materials, enhancing both sensitivity and selectivity in the extraction process. The growing interest in sorbent-based techniques is driven by the need for more efficient, environmentally friendly, and high-throughput approaches for detecting trace-level antidepressants in biological and environmental samples [16]. Sorbent-based extraction techniques encompass a range of methods, including Solid-Phase Extraction (SPE), Solid-Phase Microextraction (SPME), and emerging microextraction strategies such as Microextraction by Packed Sorbent (MEPS) and Dispersive Solid-Phase Extraction (d-SPE), as illustrated in **Figure 1**.

SPE, a well-established technique, involves passing a liquid sample through a sorbent-packed column to retain the target analytes, followed by their elution using a suitable solvent. SPE offers multiple advantages, including high selectivity, cleaner extracts, prevention of emulsion formation, reduced solvent consumption, and increased efficiency through automation. Furthermore, the availability of a wide range of sorbents such as polar, nonpolar, mixed-mode, ion-exchange, and polymeric sorbents or their combinations [17]. In contrast, SPME utilizes a coated fibre to adsorb analytes directly from the sample, eliminating the need for large solvent volumes while maintaining high sensitivity. One of the key advantages of sorbent-based approaches is their ability to minimize sample and solvent requirements while achieving high enrichment factors and improved analyte recovery. These methods also offer enhanced selectivity using tailored sorbents, which can be functionalized to target specific antidepressant compounds [18, 19]. As research continues to refine these approaches, the development of novel sorbent materials, such as magnetic and nanostructured sorbents, holds great promise for further improving the efficiency and sustainability of antidepressant analysis in biological and environmental applications.

This review aims to provide a comprehensive overview of the advancements in sorbent-based extraction techniques for the pre-concentration of antidepressant drugs. It will explore various types of sorbents, their properties, and the factors influencing their performance, such as extraction conditions, sorbent selection, and matrix interferences. Additionally, the review also discussed the application of these techniques in both clinical and environmental analysis, highlighting their potential to improve the detection and quantification of antidepressants in complex samples. Ultimately, this article seeks to provide valuable insights into the current state of sorbent-based extraction for antidepressant drug analysis, identifying challenges and opportunities for further development.

Classification of antidepressant drugs

Antidepressant drugs are classified based on their chemical structure, mechanism of action, and specific target pathways in the brain. These medications primarily regulate neurotransmitters such as serotonin, norepinephrine, and dopamine, which play crucial roles in mood regulation. The major classes of antidepressants include tricyclic antidepressants (TCAs), monoamine oxidase inhibitors (MAOIs), selective serotonin reuptake inhibitors (SSRIs), serotonin-norepinephrine reuptake inhibitors (SNRIs), and atypical antidepressants [20, 21]. TCAs are among the oldest classes of antidepressants and function by inhibiting the reuptake of serotonin (e.g., amitriptyline, imipramine, clomipramine, and doxepin – tertiary amines) and norepinephrine (e.g., desipramine, nortriptyline, and protriptyline – secondary amines), thereby increasing their availability in the synaptic cleft [22, 23]. These

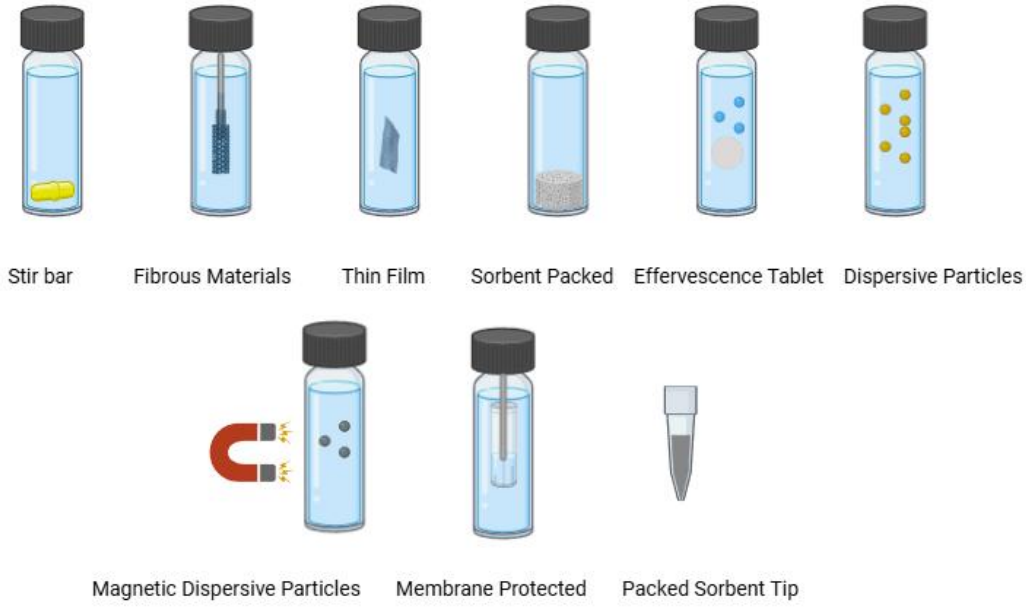

Figure 1. Variations in extraction types using sorbent materials for analytical method development

compounds share a common three-ring chemical structure, with the central ring containing seven or eight carbon atoms, along with a side chain and a terminal amine group [24]. In some cases, amitriptyline and imipramine, widely used in psychiatry, are primarily metabolized in the liver into nortriptyline and desipramine, also have an antidepressant activity [25].

TCAs have a narrow therapeutic index (50.0 to 300.0 µg L^{-1}), which increases the risk of toxicity. While TCAs are effective, their use is often limited due to significant side effects, including dry mouth, constipation, and cardiotoxicity. As a result, they are typically reserved for cases where other antidepressants are ineffective or when patients have comorbid conditions requiring sedative properties. Notably, over the past few decades, suicide cases due to poisoning have risen by 38.5%, with most poisoning-related deaths involving medications. Among antidepressants, TCAs have been reported to have the highest mortality rate [26].

Monoamine oxidase inhibitors (MAOIs) exert their pharmacological effects by inhibiting monoamine oxidase, the enzyme responsible for the breakdown of key neurotransmitters, including serotonin, norepinephrine, and dopamine. This inhibition leads to increased synaptic concentrations of these neurotransmitters, enhancing their mood-regulating effects. MAO exists in two isoforms, MAO-A and MAO-B, each with distinct substrate selectivity. MAO-A preferentially deaminates serotonin, melatonin, epinephrine, and norepinephrine, whereas MAO-B primarily metabolizes phenylethylamine and trace amines. Both isoforms contribute equally to dopamine degradation. MAOIs are categorized based on their chemical structure into several groups: hydrazines (e.g., isocarboxazid, isoniazid, nialamide, phenelzine), non-hydrazines (e.g., tranylcypromine), selective MAO-A inhibitors (e.g., moclobemide, pirlindole, toloxatone), and selective MAO-B inhibitors (e.g., rasagiline, selegiline) [27]. Due to the risk of hypertensive crises associated with tyramine-rich foods, MAOIs require strict dietary restrictions and are generally reserved for cases of treatment-resistant depression.

Selective serotonin reuptake inhibitors (SSRIs) are the most prescribed class of second-generation antidepressants, largely due to their relatively mild side effect profile and high specificity for inhibiting serotonin reuptake. They are effective in treating a broad range of mood disorders, including depression, anxiety, and obsessive-compulsive disorder. Given their favourable tolerability and safety, SSRIs are considered the first-line treatment for many patients, particularly when concerns about drug–drug interactions with other substrates arise [28]. Since their introduction, SSRIs have been widely recognized

for their therapeutic effects in depression, primarily through the modulation of monoaminergic neurotransmission. The main mechanism involves the inhibition of serotonin reuptake at the synaptic cleft, which results in increased serotonin availability and prolonged signalling. This enhancement of serotonergic activity is believed to play a key role in alleviating depressive symptoms [29].

SNRIs, such as venlafaxine and duloxetine, target both serotonin and norepinephrine reuptake. They are often prescribed for patients with major depressive disorder, particularly when accompanied by chronic pain syndromes like fibromyalgia or neuropathy. SNRIs share many advantages with SSRIs but may cause additional side effects such as hypertension in some patients. Atypical antidepressants, such as bupropion and mirtazapine, operate via unique mechanisms and are often used in patients who do not respond well to traditional classes. For instance, bupropion is a norepinephrine-dopamine reuptake inhibitor that also aids in smoking cessation, while mirtazapine enhances serotonin and norepinephrine activity through receptor antagonism and has sedative properties. These drugs expand the options available for individualized treatment, addressing specific patient needs and comorbid conditions [9, 30].

Selection of materials

Carbon-based sorbents

Carbon-based materials have emerged as highly efficient sorbents for pre-concentration techniques in the analysis of antidepressant drugs (**Table 1**). Their unique physicochemical properties, such as high surface area, tuneable porosity, chemical inertness, and ease of functionalization, make them ideal for extracting and enriching trace-level analytes from complex matrices [31]. Activated carbon (AC) is typically derived from carbon-rich precursors such as agricultural byproducts, including peanut shells, coconut shells, and wood, through processes involving carbonization and activation. Agro-industrial residues are promising alternatives to activated carbon due to their high availability, low toxicity, and adsorption capacities [32]. AC is widely used as a sorbent due to its large surface area, high porosity, and cost-effectiveness. Its hydrophobic character and ability to adsorb organic compounds make it effective for pre-concentrating antidepressant drugs from water and biological fluids [33].

Materials formulated as a fine powder or incorporated into extraction setups. Size reduction through grinding is commonly performed to produce a fine powder, enhancing surface area and facilitating uniform packing in extraction systems. Functionalization is another critical step, where chemical agents or functional groups, such as carboxylic or amine groups, are introduced to improve selectivity and adsorption efficiency for specific antidepressants. Acid treatment with agents like HNO_3 or H_2SO_4 introduces oxygenated functional groups, such as carboxyl (-COOH) and hydroxyl (-OH), on the surface, improving hydrophilicity and adsorption capacity [34].

Base activation using chemicals like KOH, NH_3, or NaOH modifies the pore structure and enhances the surface basicity, promoting interaction with acidic analytes. Thermal activation under controlled atmospheres (e.g., N_2, CO_2) optimizes pore development and tailors the textural properties for specific adsorption applications. Impregnation with metal or metal oxides, such as Fe_3O_4 or ZnO, introduces additional functionalities like magnetic or photocatalytic properties for advanced separation and degradation processes. Polymer coating involves grafting functional polymers onto the AC surface, enabling selective adsorption of target molecules based on chemical affinity [35-37].

Solvent conditioning is utilized to activate the surface of AC, typically through washing with polar (e.g. methanol) or nonpolar (e.g. hexane) solvents, depending on the physicochemical properties of the target analytes. Conditioning steps often involve sequential washing with solvents to remove impurities and stabilize the sorbent. Additionally, AC is immobilized onto solid supports, such as fibres or films, for integration into solid-phase microextraction (SPME) systems or packed into cartridges for solid-phase extraction (SPE). The primary mechanisms involved in the interaction between AC and antidepressant drugs, include hydrophobic interactions, π-π stacking, and van der Waals forces. Modifying AC with chemical agents or functional groups further enhances its selectivity and adsorption capacity, enabling its application in solid-phase extraction (SPE) and solid-phase microextraction (SPME) techniques [2, 38].

Carbon nanotubes (CNTs), including single-walled (SWCNTs) and multi-walled (MWCNTs) variants, are synthesized from carbon-rich precursors such as hydrocarbons or biomass through methods like chemical vapor deposition (CVD), arc discharge, or laser ablation [39]. CVD works by breaking down a hydrocarbon on a surface. A carbon source is heated in a furnace at 700 °C or higher, where a catalyst-coated substrate (like Fe or Ni) helps the process. Factors such as temperature, catalyst type, and hydrogen (H_2) influence the quality and purity of the resulting CNTs [40]. Materials have garnered attention for their exceptional mechanical strength, electrical conductivity, and high adsorption capacity. CNTs are often used in their pristine or functionalized

forms, typically incorporated into SPE or dispersive solid-phase microextraction (d-SPME) setups.

To enhance their compatibility and adsorption performance, several preparation techniques have been employed. Acid treatment using concentrated acids such as nitric (HNO_3) or sulfuric acid (H_2SO_4) introduces oxygen-containing functional groups, such as carboxyl (-COOH) and hydroxyl (-OH), improving hydrophilicity and interaction with analytes [41, 42]. Surface oxidation, achieved through chemical or plasma methods, generates additional active sites for adsorption. Polymer grafting facilitates the attachment of functional polymers or coatings to tailor the chemical properties of the CNT surface. Decoration with metal or metal oxide nanoparticles, such as Fe_3O_4 or Au, imparts magnetic or catalytic properties, enhancing separation and interaction with specific compounds [43]. Covalent or non-covalent functionalization introduces specific functional groups or molecules, such as amino (-NH_2) or thiol (-SH) groups, to improve selectivity for target analytes through specific binding interactions [44, 45]. These approaches enable the modification of CNTs to serve as versatile and efficient sorbents in analytical and environmental applications.

The adsorption of aromatic antidepressants like amitriptyline and paroxetine onto CNTs is driven primarily by π-π interactions between the aromatic structures of the drugs and the graphitic surface of the CNTs [46]. Functionalized CNTs, modified with carboxylic or hydroxyl groups, enhance dispersibility in aqueous media and introduce specific interactions such as hydrogen bonding, improving the selectivity and efficiency of the extraction process [47]. Challenges associate CNTs include their tendency to aggregate due to strong van der Waals forces, which can limit their effective surface area, and potential difficulties in separating and recovering CNTs from the sample matrix, especially in dispersive techniques [48, 49]. Additionally, the high cost of CNT synthesis and concerns about their environmental and biological safety may restrict their broader application.

Graphene and its derivatives, including graphene oxide (GO) and reduced graphene oxide (rGO), are typically synthesized from graphite using methods such as chemical exfoliation, Hummers' method, or chemical vapor deposition (CVD). Materials exhibit superior adsorption properties due to their two-dimensional structure and high surface area. Several preparation methods enhance their compatibility as sorbents. Oxidation of graphene using agents like concentrated sulfuric acid and potassium permanganate produces graphene oxide (GO), introducing oxygen-containing functional groups (e.g., carboxyl, hydroxyl), which increase hydrophilicity and adsorption capacity. Reduction of GO to rGO using chemical (e.g., hydrazine, ascorbic acid) or thermal methods restores the conductivity and structural integrity, while maintaining some functional groups for enhanced adsorption [50, 51].

Polymer functionalization involves grafting polymers such as polyethyleneimine or polyaniline onto the graphene surface, allowing selective adsorption through specific interactions. Metal or metal oxide decoration incorporates nanoparticles (e.g., Au, Ag, Fe_3O_4) onto graphene, enhancing adsorption by providing additional active sites and improving specific interactions with target analytes. Intercalation with organic or inorganic molecules involves inserting specific molecules between graphene layers, which can modify the surface properties and enhance selective sorption [52].

For extraction applications, graphene-based sorbents are commonly formulated as dispersions for dispersive solid-phase extraction (d-SPE) or incorporated into SPE cartridges, taking advantage of their high surface area and versatile functionalization options [53]. The adsorption of antidepressants onto graphene-based materials is facilitated by mechanisms such as π-π stacking with the aromatic structures of the drugs, hydrogen bonding with oxygen-containing functional groups in GO, and electrostatic interactions depending on the drug's charge and the surface properties of the sorbent [54].

Despite their excellent adsorption properties, challenges in using graphene-based materials include their potential aggregation in aqueous systems, which can reduce the accessible surface area, and the complex synthesis and functionalization processes required to enhance dispersibility and selectivity. Additionally, the high cost of production and the potential environmental impact of graphene derivatives may pose limitations for large-scale applications. The incorporation of magnetic nanoparticles into carbon-based materials combines the high adsorption capacity of carbon with the magnetic responsiveness of iron oxides, enabling easy separation using external magnets [55].

Magnetic graphene oxide and magnetic CNTs have been successfully employed for the extraction of antidepressants from environmental and biological samples. Magnetic nanoparticles are highly valued for their large surface area, ease of surface modification, and recyclability, making them ideal adsorbents in the sorbent-based extraction [56]. Superparamagnetic nanoparticles like Fe_3O_4 are magnetically responsive but retain no residual magnetism once the field is removed, enabling easy extraction without centrifugation or filtration [57].

Carbon dots (CDs) are synthesized from a variety of carbon-rich precursors, such as organic compounds, biomass, or carbon-based polymers, through methods like hydrothermal carbonization, laser ablation, or chemical oxidation [58]. CDs are a novel class of carbon-based nanomaterials that exhibit photoluminescence and tuneable surface properties. Their small size, high surface-to-volume ratio, and ease of surface modification make them attractive for pre-concentration applications. CDs are often formulated as dispersions or incorporated into composite materials to serve as sorbents in techniques such as dispersive solid-phase extraction (d-SPE) or fluorescence-based detection systems. Several preparation methods enhance their compatibility and adsorption performance. Surface functionalization with carboxyl (-COOH), amine (-NH_2), or hydroxyl (-OH) groups through oxidation or chemical treatments improves their hydrophilicity and increases the number of active sites for adsorption. Covalent or non-covalent grafting of polymers such as polyethyleneimine or polyvinyl alcohol onto the CD surface introduces selective chemical functionalities, enhancing their affinity for target analytes. Doping with heteroatoms like nitrogen, sulphur, or phosphorus modifies the electronic properties of CDs, boosting their interaction with specific molecules and improving adsorption efficiency [59].

Metal nanoparticle incorporation involves loading CDs with metal nanoparticles (e.g., Ag, Au, Fe_3O_4), imparting additional catalytic or magnetic properties, thereby expanding their functionality as sorbents. Hydrothermal or solvothermal synthesis enables the incorporation of various functional molecules into the CDs' structure, allowing fine control over their size, surface charge, and reactivity, which further enhances their ability to adsorb a variety of compounds [60]. CDs functionalized with specific ligands or polymers can selectively adsorb antidepressants like duloxetine and citalopram, offering promising avenues for fluorescence-based detection. The adsorption of antidepressants onto CDs is facilitated by mechanisms such as hydrogen bonding, electrostatic interactions, and hydrophobic effects, enhanced by the functional groups or ligands present on the CDs' surface.

Porous carbon materials, such as mesoporous carbon and metal-organic framework (MOF)-derived carbons, are synthesized from carbon-rich precursors, including organic polymers or MOFs, through processes like carbonization and activation [61, 62]. These materials are typically formulated as powders or incorporated into SPE cartridges, leveraging their hierarchical porosity and high surface area for efficient adsorption [63]. Solvothermal synthesis is a common method where metal salts and organic ligands are reacted in a solvent under elevated temperature and pressure to form highly crystalline MOFs, optimizing their structural properties for specific adsorption tasks. Post-synthesis functionalization introduces specific functional groups (e.g., amine, carboxyl) to the MOF structure through reactions with various chemical agents, enhancing interaction with target analytes and improving selectivity. Doping with metals or metal nanoparticles involves incorporating additional metals (e.g., Cu, Zn, Fe) or metal nanoparticles into the MOF structure, which can provide additional active sites and catalytic properties, enhancing adsorption capacity and selectivity. Hydrothermal synthesis employs water as a solvent to promote the formation of MOFs, allowing for the fine-tuning of structural and chemical properties by controlling reaction conditions such as temperature, pressure, and pH [64].

Composite formation involves incorporating MOFs into other materials, such as carbon nanotubes, graphene, or polymers, to combine their sorptive properties with the advantages of the composite materials, improving stability and expanding the range of adsorbates that can be captured. The primary mechanisms driving the adsorption of bulky antidepressants onto porous carbon materials include pore-filling effects, π-π stacking interactions, and van der Waals forces, which facilitate the selective pre-concentration of these drugs from complex matrices like urine, serum, and wastewater [65]. Despite their advantages, challenges in using porous carbons include the potential for fouling by matrix components, which can block the pores and reduce adsorption efficiency, as well as the intricate and energy-intensive synthesis processes required to achieve the desired pore structure and functionalization. Additionally, balancing the material's hydrophobic and hydrophilic properties to optimize selectivity for specific antidepressants can be complex.

Combining carbon-based materials with other sorbents, such as polymers, silica, or metallic nanoparticles, creates hybrid sorbents with improved functionality. For instance, polymer-coated GO or CNTs can enhance selectivity toward specific antidepressants while retaining the high adsorption capacity of the carbon matrix. These hybrid materials have demonstrated superior performance in multi-residue analysis and matrix effect reduction. Previous study reveals that m-SPE method using magnetic poly(styrene-co-divinylbenzene)/multiwalled CNTs composite enabled efficient and reusable solid-phase extraction of antidepressants from human urine, achieving >89.5% recovery, low detection limits (0.014–0.041 μg/mL), and high precision in capillary electrophoresis analysis [66, 67].

Table 1. Carbon based materials used as adsorbent in extraction procedure for determining antidepressant drugs

Type	Source	Functionalisation	Method	Extraction Mode	Dosage (mg)	Target Analytes	Instrument	References
Activated carbon	Commercial	Bare	Direct	SPE	5	Amit, Nort	UV-Vis	[36]
	Synthesize	Fe_3O_4	Co-precipitate	m-d-SPE	1000	Esci, Flu, Paro	HPLC-DAD	[68]
	Synthesize	ZnCoAl	Co-precipitate	SPE	100	Flu	HPLC	[35]
	Synthesize	Fe_3O_4	Acid treated	m-SPE	10	Amit, Sert, Flu	HPLC-UV	[69]
	Synthesize	Bare	Pyrolysis	SPE	500	Cit	UV-Vis	[70]
	Synthesize	Fe_3O_4	Alkaline treated	m-SPE	500	Paro	HPLC-DAD	[71]
Graphene	Commercial	Bare	Electrochemical	SPME	-	Clo, Des, Imip	GC-FID	[72]
	Commercial	Bare	Sol-gel	FPSE	-	Amit, Clo, Flu, Paro, Ven	HPLC-UV	[73]
	Synthesize	Fe_3O_4	Hummer	m-SPE	50	Cit, Flu	HPLC-DAD	[12]
	Synthesize	Fe_3O_4	Hummer	SPE	1000	Burp, Sert	LC-MS	[74]
	Synthesize	Fe_3O_4	Co-precipitate	m-SPE	20	Amit, Clo, Imip, Flu	GC-MS	[75]
	Synthesize	Fe_3O_4	Exfoliation and oxidation	m-SPE	1000	Cit	UV-Vis	[76]
	Synthesize	Polyester	Surface grafting	µ-SPE	1.5	Des, Ven	HPLC-FLD	[64]
	Synthesize	PEDOT	Electrodeposition	SPME	20	Amit, Imi, Desi, Map, Nor, Sert	GC-FID	[77]
Carbon nanotubes	Commercial	Fe_3O_4	Acid treated	SPE	14	Flu	UV-Vis	[78]
	Commercial	β-cyclodextrin	Sol-gel	HF-SPME	-	Flu, Nflu	HPLC-DAD	[79]
	Commercial	Glycine	Sol-gel	HF-SPME	-	Des, Ven	HPLC-DAD	[80]
	Commercial	Bare	Acid treatment	SPE	-	Amit	UV-Vis	[44]
	Commercial	-	Salinization	SPME	200	Flu	FS	[81]
	Synthesize	-	Co-precipitate	SPME	0.6	Amit, Chlo	HPLC-UV	[82]
Carbon dot	Synthesize	Fe_3O_4	Emulsion	m-SPE	20	Cit, Sert, Desi	CD-IMS	[83]
	Synthesize	AuNPs	Co-precipitate	SPE	-	Cit, Flu, Sert	UV-Vis	[84]
	Synthesize	PET	Pyrolysis	SPE	100	Flu	UV-Vis	[85]
MOF-carbon based	Synthesize	Fe_3O_4	Step-by-step assembly	m-SPE	5	Amit, Imip	HPLC-UV	[86]
	Synthesize	ZIF-8	Electrochemical	TFME	2	Flu	Fluorimetry	[87]
	Synthesize	Fe_3O_4	One pot	m-SPE	10	Amit, Cit, Flu, Imip, Sert, Ven	HPLC-UV	[88]
	Synthesize	Fe_3O_4	Electrospinning	TFME	-	Amit, Nort	HPLC-UV	[89]

Amit: Amitriptyline hydrochloride; AuNPs: Gold nanoparticles, CD-IMS: Corona Discharge Ion Mobility Spectrometry; Cit: Citalopram; Desi: Desipramine; Esci: Escitalopram; Fe_3O_4: Magnetite nanoparticles; Flu: Fluoxetine; FS: Fluorescent Spectrometry; GC-FID: Gas Chromatography-Flame Ionisation Detector; GC-MS: Gas Chromatography-Mass Spectrometry; HF-SPME: Hallow fibre solid phase microextraction, HPLC: High Performance Liquid Chromatography; HPLC-DAD: High Performance Liquid Chromatography Diode Array Detector; Imip: Imipramine, LC-MS: Liquid Chromatography-Mass Spectrometry; m-d-SPE: magnetic dispersive solid phase extraction; m-SPE: magnetic solid phase extraction; Nort: Nortriptyline; Paro: Paroxetine, PEDOT: Poly(3,4-ethylenedioxythiophene); Sert: Sertaline; SPME: solid phase microextraction; TFME: Thin film microextraction, UV-Vis: Ultraviolet-Visible Light; Ven: Venlafaxine; ZIF: Zeolitic imidazolate framework

Natural-based polymers

Natural-based polymers offer a sustainable and eco-friendly alternative to synthetic sorbents for the pre-concentration of antidepressant drugs. Derived from renewable sources such as plants, animals, and microorganisms, these polymers offer bio-compatibility, biodegradability, and cost-effectiveness [90]. Their tuneable surface chemistry and ability to form functionalized derivatives make them versatile for applications in solid-phase extraction (SPE), liquid-phase microextraction (LPME), and related techniques. Their adsorption mechanisms primarily involve hydrogen bonding, electrostatic interactions, hydrophobic forces, π-π stacking, and ion exchange, depending on the functional groups present in the polymer structure [91].

Cellulose, one of the most abundant natural polymers, serves as an excellent sorbent due to its hydrophilic surface, high mechanical strength, and chemical versatility. Cellulose-based materials have been used in SPE cartridges and filter papers for sample preparation in analytical workflows. It relies on hydrogen bonding and dipole-dipole interactions for drug adsorption. Functionalized cellulose derivatives, such as carboxylate or aminated forms, introduce additional ionic interactions that enhance selectivity [92]. However, cellulose's limited affinity for nonpolar drugs and its tendency to swell in aqueous environments require structural modifications to improve its performance. Similarly, chitosan, derived from the deacetylation of chitin, is a biopolymer with exceptional adsorption properties which contains amine (-NH_2) and hydroxyl (-OH) groups, interacts strongly with anionic antidepressants such as fluoxetine and sertraline through electrostatic interactions, hydrogen bonding, and van der Waals forces [93]. Chitosan's ability to chelate metal ions further increases its adsorption potential, yet its low solubility at neutral and basic pH levels limits its versatility. The challenge lies in optimizing its functionalization to maintain stability while ensuring high selectivity for target analytes [94].

Alginate, a polysaccharide derived from brown algae, primarily engages in ion exchange with cationic antidepressants due to its carboxyl (-COO^-) groups. Its adsorption efficiency is pH-dependent, as protonation or deprotonation of functional groups affects drug binding. Alginate's ability to coordinate with metal ions enhances its selectivity, but its weak mechanical strength and excessive swelling behaviour necessitate cross-linking for improved stability. A novel, low-cost alginate-based hydrogel device supported in a polypropylene hollow fibre, as documented by Guzella et al. enabled effective and selective extraction of fluoxetine and norfluoxetine from human plasma, excluding over 95% of proteins and achieving quantifiable recoveries with satisfactory precision for HPLC-FD analysis. [95, 96]. Likewise, starch and its derivatives, which contain hydroxyl groups capable of forming hydrogen bonds with polar antidepressants, exhibit enhanced adsorption efficiency when modified with functional groups such as carboxyl or amine moieties. However, the hydrophilic nature of native starch limits its ability to capture nonpolar drugs, requiring strategies that balance polarity to optimize extraction capabilities [97, 98].

Proteins such as gelatine, casein, and silk fibroin possess multiple reactive functional groups, allowing them to interact with antidepressant drugs through hydrogen bonding, electrostatic interactions, and covalent bonding. For example, casein's negatively charged residues facilitate interactions with cationic drugs, while silk fibroin enables hydrophobic and π-π interactions with aromatic drug molecules. Despite their versatility, proteins suffer from poor mechanical strength and susceptibility to degradation, which necessitates their incorporation into composite materials to improve their stability and reusability [99].

Natural rubber, characterized by its hydrophobic nature, is particularly suited for extracting lipophilic antidepressants through van der Waals forces and hydrophobic interactions. While it offers a renewable and cost-effective alternative, its efficiency for hydrophilic drugs is limited, requiring functionalization with polar groups such as carboxyl (-COOH) or amine (-NH_2) to enhance selectivity [100, 101]. To date, no specific study has reported the potential use of natural rubber for the extraction or removal of antidepressants.

Despite the numerous advantages of natural-based polymers, challenges such as structural instability, selective adsorption, and efficient desorption must be addressed to optimize their use in analytical workflows. Functionalization strategies must be carefully tailored to enhance adsorption efficiency while maintaining the polymers' sustainability. Future research should focus on developing hybrid materials that combine different natural polymers or integrate nanomaterials to enhance selectivity and mechanical properties. By overcoming these challenges, natural-based polymer sorbents can serve as viable and environmentally friendly alternatives for pre-concentrating antidepressant drugs in various analytical applications [102, 103]. Natural polymer-based materials used as adsorbent are summarized in **Table 2**.

Table 2. Natural and synthetic polymer-based materials used as adsorbent in extraction procedure for determining antidepressant drugs

Type	Source	Functionalisation	Method	Extraction Mode	Dosage (mg)	Target Analytes	Instrument	References
Alginate	Commercial	-	Hydrogel	SPME	-	Flu, Nflu	HPLC-FD	[104]
Cellulose	Commercial	-	Drop casting	SPE	-	Ami, Imi, Desi, Tri	HPLC-UV	[105]
	Commercial	PTHF	Sol gel	FPSE	-	Ami, Dul, Flu, Vil	HPLC-PDA	[106]
	Commercial	Octanol	Impregnate	RPD	-	Ami, Flu, Ven	GC-MS	[107]
	Commercial	MMT/PS	Wet deposition	MEPS	-	Flu	Fluorimetry	[108]
	Commercial	Carbowax	Sol gel	FPSE	-	Ami, Cit, Clo, Flu, Par, Sert, Ven	HPLC-PDA	[109]
	Kapok fiber	-	Untreated	SPE	20	Ami, Cit, Imi, Flu, Sert, Ven	HPLC-UV	[110]
Chitosan	Commercial	β-cyclodextrin	Co-precipitate	SPE	100	Desi	HPLC	[111]
	Commercial	β-cyclodextrin	Co-precipitate	m-SPE	100	Ami	HPLC-UV	[112]
	Commercial	Fe_3O_4	Alkaline treatment	m-SPE	25	Flu	Fluorimetry	[113]
	Commercial	GO	Acidic treatment	TFME	-	Flu	HPLC-UV	[114]
	Commercial	GO and Fe_3O_4	Acidic treatment	SPE	20	Flu	PDA	[115]
Polyaniline	Commercial	-	Polymerization	SPE	5	Flu, Nflu	LC-FD	[116]
Polydimethylsiloxane	Commercial	-	Polymerization	SBSE	-	Cit, Dulo, Flu, Mir, Par, Sert	LC-UV	[117]
	Commercial	-	-	SPME	-	Ami, Clo, Tri	GC-MS	[118]
	Commercial	-	Co-polymerization	SPME	-	Cit, Flu, Fluv, Sert, Ven	GC-MS	[119]
Poly(methacrylic acid)	Commercial	-	Co-polymerization	SPE	70	Ami, Clo, Dox, Imi, Nor	HPLC-DAD	[120]
Polypyrrole	Commercial	Fe_3O_4	Co-precipitate	D-μ-SPE	10	Cit, Sert	HPLC-UV	[121]
	Commercial	PDA	In-situ reduction	MEPS	2	Ami, Cit	GC-MS	[122]
	Commercial	-	Doped	SPME	-	Alp, Imi, Sert	IMS	[123]
	Commercial	-	Silanization	IT-SPME	-	Flu, Nflu	LC-FD	[124]
	Commercial	-	Silanization	SPME	35	Imi	IMS	[125]
Polystyrene	Commercial	Fe_3O_4	Co-precipitate	SS-LPME	20	Ami, Sert	GC-MS	[126]
	Commercial	Fe_3O_4	Co-precipitate	D-μ-SPE	-	Ami, Sert	GC-MS	[127]
	Commercial	-	Dipping	μ-SPE	-	Ami, Cit	CE-MS	[128]
Polythiophene	Commercial	-	Electropolymerization	SPME	-	Cit, Flu, Par, Sert	LC-UV	[129]
Polyvinyl alcohol	Commercial	g-C_3N_4	Electrospinning	μ-SPE	4	Clo, Trim	GC-FID	[130]

Amit: Amitriptyline hydrochloride; AuNPs: Gold nanoparticles, CD-IMS: Corona Discharge Ion Mobility Spectrometry; Cit: Citalopram; Desi: Desipramine; Esci: Escitalopram; Fe_3O_4: Magnetite nanoparticles; Flu: Fluoxetine; FS: Fluorescent Spectrometry; GC-FID: Gas Chromatography-Flame Ionisation Detector; GC-MS: Gas Chromatography-Mass Spectrometry; HF-SPME: Hallow fibre solid phase microextraction, HPLC: High Performance Liquid Chromatography; HPLC-DAD: High Performance Liquid Chromatography Diode Array Detector; Imip: Imipramine, LC-MS: Liquid Chromatography-Mass Spectrometry; m-d-SPE: magnetic dispersive solid phase extraction; m-SPE: magnetic solid phase extraction; Nort: Nortriptyline; Paro: Paroxetine, PEDOT: Poly(3,4-ethylenedioxythiophene); Sert: Sertaline; SPME: solid phase microextraction; TFME: Thin film microextraction, UV-Vis: Ultraviolet-Visible Light; Ven: Venlafaxine; ZIF: Zeolitic imidazolate framework

Synthetic-based polymers

Variation of synthetic polymer-based materials used as adsorbent are summarized in **Table 3**. Polystyrene-Divinylbenzene (PS-DVB) is a highly porous sorbent synthesized by polymerizing styrene with divinylbenzene. It interacts with antidepressants primarily through hydrophobic interactions and π-π stacking between its benzene rings and the aromatic structures of the drugs. Functionalization with sulfonic acid (-SO_3H) or amino (-NH_2) groups enhances selectivity toward specific antidepressants [131]. PS-DVB offers excellent stability and a large surface area but suffers from poor wettability in aqueous samples. A major challenge is achieving selectivity for structurally similar drugs while minimizing matrix interferences [132].

Molecularly Imprinted Polymers (MIPs) are tailored sorbents synthesized by polymerizing functional monomers around a template molecule, creating highly selective recognition sites. The adsorption mechanism involves hydrogen bonding, ionic interactions, and hydrophobic effects that enable precise binding of antidepressants [133]. Methacrylic acid (MAA) and acrylamide are commonly used monomers to introduce specific functional groups. MIPs provide exceptional selectivity, but their synthesis is time-consuming, and incomplete template removal may hinder adsorption efficiency. The primary challenge lies in maintaining structural integrity and reusability over multiple extraction cycles [134].

Polyacrylamide (PAM) is synthesized through the polymerization of acrylamide monomers, forming a hydrophilic network that interacts with antidepressants via hydrogen bonding and dipole interactions. It can be functionalized with carboxyl (-COOH) or sulfonic acid (-SO_3H) groups to improve adsorption efficiency. PAM is well-suited for aqueous environments, offering good compatibility with biological samples; however, its adsorption capacity is relatively low. One significant challenge is its tendency to swell in water, which can reduce extraction efficiency and hinder sorbent reuse. Polyvinylpyrrolidone (PVP) is an amphiphilic polymer derived from the polymerization of N-vinylpyrrolidone. It primarily adsorbs antidepressants through hydrogen bonding and dipole-dipole interactions, particularly with nitrogen and oxygen-containing functional groups. PVP can be blended with other polymers or cross-linked to enhance its adsorption capacity. It is biocompatible and highly soluble in various solvents, but its moderate sorption capacity can limit its effectiveness. Additionally, its mechanical strength is relatively low, posing a challenge in maintaining structural stability over prolonged use [135, 136].

Poly(methyl methacrylate) (PMMA) is a robust sorbent synthesized via free radical polymerization of methyl methacrylate monomers [137]. Antidepressant adsorption on PMMA is driven by hydrophobic and van der Waals interactions. Functionalization with hydroxyl (-OH) or carboxyl (-COOH) groups can enhance affinity for polar drugs. PMMA is chemically resistant and stable but lacks strong selectivity for specific antidepressants. A key challenge is its non-selective nature, which may require additional modifications to improve specificity [138].

Polyethylene glycol-based polymers (PEG) are synthesized by cross-linking PEG chains with functional monomers, forming a hydrophilic sorbent. The extraction of antidepressants relies on hydrogen bonding and hydrophobic interactions. Functionalization with amine (-NH_2) or sulfonic acid (-SO_3H) groups improves selectivity [139, 140]. PEG-based sorbents are biocompatible and environmentally friendly but offer lower adsorption capacities than other polymeric materials. Their primary challenge is achieving sufficient drug retention while maintaining a balance between hydrophilicity and selectivity.

Polyaniline (PANI) is a conductive polymer synthesized through oxidative polymerization of aniline monomers. It interacts with antidepressants via electrostatic forces, π-π interactions, and hydrogen bonding. Functionalization with sulfonic acid (-SO_3H) groups enhances its affinity for cationic drugs. For example, a bifunctional sulfonated polyaniline nanofiber mat (NFM) synthesized via oxidative polymerization exhibited high adsorption capacity and reusability for extracting target drugs from water and biological fluids, primarily through hydrogen bonding and ion-exchange interactions. The sorbent enabled rapid, efficient extraction with low detection limits, high recoveries, and minimal adsorbent usage, demonstrating excellent stability over 20 reuse cycles. PANI's advantages include tuneable functionality and excellent electrochemical properties, but it is prone to environmental degradation [141].

Polypyrrole (PPy) is another conductive polymer synthesized through the oxidative polymerization of pyrrole monomers. It adsorbs antidepressants through hydrogen bonding and π-π interactions. Functionalization with carboxyl (-COOH) or sulfonic acid (-SO_3H) groups can further enhance its selectivity. PPy offers good adsorption capacity and conductivity, making it suitable for electrochemical applications. However, it is susceptible to oxidation, which can limit its long-term stability. A previous study documented the synthesis and characterization of PPy/Fe_3O_4 nanocomposites with different dopants,

showing that the sodium-perchlorate-doped version delivered superior extraction of citalopram and sertraline. Using 10 mg of this sorbent under optimized D-μ-SPE conditions (pH 9, 7 min adsorption, 120 μL 0.06 mol L^{-1} HCl in methanol, 2 min elution) and HPLC-UV detection gave linearity from 1–800 μg L^{-1}, detection limits down to 0.2 μg L^{-1}, recoveries of 93–99 %, and successful analysis of human urine and plasma. Other study introduced electromembrane surrounded solid-phase microextraction (EM-SPME) using a PPy-coated fibre as both the cathode and sorbent for the extraction of amitriptyline and doxepin from human blood and urine. The method, optimized for variables such as pH, voltage, and extraction time, achieved low detection limits (0.05–0.3 ng mL^{-1}), high precision, good linearity (up to 50 ng mL^{-1}), and clean chromatograms suitable for analysing complex biological matrices. [121, 142, 143].

Analytical performance

Activated carbon is a well-established sorbent characterized by a high surface area (500–2000 m^2/g) and strong hydrophobic interactions, making it effective for antidepressant extraction. The adsorption mechanism is mainly driven by π-π interactions, van der Waals forces, and hydrogen bonding. AC-based sorbents typically exhibit linearity in the range of 0.1–500 ng/mL, with detection limits as low as 0.2 ng/mL. The recovery rates are generally 85–99%, depending on drug structure and matrix composition. However, strong adsorption forces can hinder desorption, affecting regeneration, which is typically limited to 5–10 cycles. AC's main drawback is its non-selective adsorption, which can lead to matrix interferences and lower extraction specificity for structurally similar antidepressants. This non-specificity may also introduce a higher risk of bias in quantification, especially when co-eluting compounds compete for the same active sites on the sorbent [68, 144].

Graphene and graphene oxide (GO) are highly efficient sorbents due to their large surface area (~2600 m^2/g), functional groups (-OH, -COOH, -O-), and strong π-π stacking interactions with antidepressant molecules. These sorbents exhibit linear ranges of 0.05–500 ng/mL, with LOD values as low as 0.005 ng/mL. Recovery rates typically range from 88–99%, depending on the functionalization of graphene or sample types. A major advantage of graphene is its high sorption capacity (up to 350 mg/g) and better selectivity compared to AC [72-77]. However, graphene tends to aggregate, which can reduce its extraction efficiency, requiring functionalization with polymers or nanoparticles for better dispersion. Despite these advantages, regeneration remains limited (~5–10 cycles) due to structural degradation over repeated use [145, 146].

CNTs, including single-walled (SWCNTs) and multi-walled (MWCNTs), possess a unique cylindrical nanostructure with high adsorption capacities (~200–300 mg/g) due to π-π interactions and hydrophobic forces. They provide excellent linearity (0.05–500 ng/mL) and low detection limits (0.001–1.5 ng/mL), making them ideal for trace-level antidepressant detection. Recovery values typically range from 80–110%, ensuring efficient extraction performance [78-82]. However, CNTs suffer from aggregation and irreversible adsorption, which reduces their reusability to about 5–8 cycles unless surface modifications (e.g., carboxylation or amination) are applied [147]. Another limitation is difficulty in dispersion, which affects extraction efficiency in aqueous samples. Thus, it preferred used as fibre types rather than free fine particles.

Carbon dots (CDs) are a new class of carbon-based nanomaterials with tuneable surface chemistry and excellent fluorescence properties. CDs interact with antidepressants via hydrogen bonding, electrostatic interactions, and π-π stacking, providing linearity in the range of 0.1–250 ng/mL, with LOD values around 0.05–1 ng/mL. While their sorption capacity (~100–200 mg/g) is lower than graphene or CNTs, CDs offer high selectivity and fast adsorption kinetics, making them suitable for rapid drug extraction. Recovery rates typically fall between 90–110%, but reusability is limited to 4–8 cycles due to surface oxidation and reduced binding efficiency over time. CDs exhibit challenges such as batch-to-batch variability during synthesis, interference from complex sample matrices, and fluorescence instability due to photobleaching, all of which can compromise their reliability and performance in microextraction applications [148]. CDs also in many attempts formulate with polymers or metal ions to enhance their adsorption performance for specific antidepressants.

MOFs are hybrid materials consisting of metal ions and organic linkers, offering ultra-high porosity (~5000 m^2/g) and tuneable functional groups. They are particularly effective for antidepressant extraction due to hydrogen bonding, electrostatic interactions, and size-selective adsorption mechanisms. MOF-based sorbents provide excellent linearity (0.01–500 ng/mL) and low detection limits (0.05–5 ng/mL), compared to conventional carbon-based materials. Recovery values are typically above 95%, with sorption capacities exceeding 400 mg/g, making MOFs one of the most efficient sorbents for antidepressants. Their key advantage is selectivity, which can be enhanced by modifying the organic ligands. However, MOFs suffer from poor chemical stability, and their regeneration is often limited to 10–15 cycles before structural degradation [87-89].

Table 3. Analytical performance of sorbent phase extraction using carbon-based materials for determining antidepressant drugs

Type	Extraction Mode	Target Analyte	Sample Type	Detection Limit	Recovery	RSD	Reference
Activated carbon	SPE	Amit, Nort	Water	0.35-1.83[d]	72-92	<10	[68]
	m-SPE	Amit, Sert, Flu	Biological fluids	1-4[d]	92-108	<8	[69]
	m-SPE	Paro	Water	0.17[a]	99	<1	[71]
	BAμE	Ami, Dos, Imi, Mia, Mir, Tri	Urine	0.2-1.6[a]	<12.3	<13.9	[144]
	FPSE	Ami, Flu, Vlz, Dul	Urine	0.38	95-105	4.8	[106]
Graphene	SPME	Desi, Imi, Clo	Plasma, Urine, Milk	0.10 to 0.35	-	<14	[72]
	FPSE	Amit, Clo, Flu, Paro, Ven	Urine	150	25-67	<14	[73]
	SPE	Burp, Sert	Water	-	98	-	[74]
	m-SPE	Amit, Clo, Imip, Flu	Plasma, Urine	0.66-1.03[b]	55-65	<6	[75]
	m-SPE	Cit	Water	-	98	-	[76]
	SPME	Amit, Imi, Desi, Map, Nor, Sert	Biological fluids	0.005-0.025[c]	-	<9	[77]
Carbon nanotubes	UA-DMSPE	Desi, Sert, Cit	Urine, Plasma	0.6-1.5	94-102	<5.1	[83]
	SPME	Flu	Urine	0.06[a]	-	<3	[78]
	HF-SPME	Flu, Nflu	Biological fluids, Water	0.3-0.4[d]	89-92	<10	[79]
	HF-SPME	Des, Ven	Biological fluids, Water	0.03-0.07[d]	86-91	<6	[80]
	SPME	Flu	Wastewater	0.001[c]	96	<1	[81]
	SPME	Amit, Chlo	Water	3.13-3.60[c]	92-110	<7	[82]
Carbon dot	m-SPE	Cit, Sert, Desi	Biological fluids	0.6-1.5[d]	94-102	<5	[83]
	SPE	Cit, Flu, Sert	Biological fluids, Urine	0.1[e]	96-102	<3	[84]
	SPE	Flu	Water	-	95	-	[85]
MOF-carbon based	m-SPE	Amit, Imip	Water, Plasma, Urine	2-4[c]	57-66	<6	[86]
	TFME	Flu	Biological Fluids	0.5[d]	77-97	<14	[87]
	m-SPE	Amit, Cit, Flu, Imip, Sert, Ven	Plasma, Urine	1.1-2.9[d]	93-108	<6	[88]
	TFME	Amit, Nort	Plasma, Urine	0.06-0.3[c]	91-100	<5	[89]

[a]μg/mL; [b] mg/mL; [c] μg/L; [d]ng/mL; [e] μM; Amit: Amitriptyline hydrochloride; AuNPs: Gold nanoparticles, CD-IMS: Corona Discharge Ion Mobility Spectrometry; Cit: Citalopram; Desi: Desipramine; Esci: Escitalopram; Fe_3O_4: Magnetite nanoparticles; Flu: Fluoxetine; FS: Fluorescent Spectrometry; GC-FID: Gas Chromatography-Flame Ionisation Detector; GC-MS: Gas Chromatography-Mass Spectrometry; HF-SPME: Hallow fibre solid phase microextraction, HPLC: High Performance Liquid Chromatography; HPLC-DAD: High Performance Liquid Chromatography Diode Array Detector; Imip: Imipramine, LC-MS: Liquid Chromatography-Mass Spectrometry; m-d-SPE: magnetic dispersive solid phase extraction; m-SPE: magnetic solid phase extraction; Nort: Nortriptyline; Paro: Paroxetine, PEDOT: Poly(3,4-ethylenedioxythiophene); Sert: Sertaline; SPME: solid phase microextraction; TFME: Thin film microextraction, UV-Vis: Ultraviolet-Visible Light; Ven: Venlafaxine; ZIF: Zeolitic imidazolate framework

Cellulose-based sorbents typically provide linearity in the range of 0.5–250 ng/mL, with detection limits (LOD) can achieved up to 5 ng/mL. Recovery rates range from 90% to 120%, depending on the degree of functionalization and the sample matrix. Despite its good biodegradability and moderate adsorption capacity (~100–200 mg/g), cellulose suffers from low hydrophobicity and weak selectivity, making it less effective for non-polar antidepressants. Bias produced seem higher for biological compared to water samples [105-110]. Regeneration is possible for 5–10 cycles but swelling in aqueous media can reduce long-term efficiency.

PDMS-DVB is a crosslinked polymer widely used in solid-phase extraction (SPE) and microextraction techniques due to its hydrophobicity and π-π interactions with aromatic antidepressants. It exhibits excellent linearity in the range of 0.05–500 ng/mL, with detection limits as low as 0.01 ng/mL. Recovery values range from 80–120%, with an adsorption capacity of ~250–350 mg/g, making it highly efficient. PDMS-DVB has superior chemical and thermal stability, allowing regeneration for up to 20 cycles without significant loss in performance [149]. However, it shows low selectivity toward highly polar antidepressants, necessitating functionalization with polar groups for improved extraction efficiency. This evident observed through high bias for inter or intra-assay (**Table 4**).

PMMA is a hydrophobic polymer with ester (-$COOCH_3$) functional groups, contributing to hydrophobic interactions and weak hydrogen bonding with antidepressants. It provides linearity in the range of 0.05–400 ng/mL, with LOD values as low 0.03 ng/mL. Recovery values range from 85–97%, and adsorption capacity (~200–300 mg/g) is relatively high. PMMA is particularly useful for extracting non-polar and weakly polar antidepressants but has limited efficiency for highly polar compounds [120, 150]. It is chemically stable, allowing regeneration for 8–12 cycles. However, low surface area and weak selectivity require modification (e.g., copolymerization with functional monomers) to enhance performance [151].

PPy, another conductive polymer, provides strong π-π interactions and electrostatic interactions, leading to high affinity toward antidepressant drugs. It offers linearity in the range of 0.01–500 ng/mL, with low LOD values of 0.02–2 ng/mL. Recovery rates are among the best, ranging from 88–120%, with an adsorption capacity of ~350–500 mg/g. PPy is highly stable and selective, particularly for tricyclic antidepressants and cationic drugs [121-125]. However, it suffers from poor dispersibility and requires composite formation with other materials (e.g., graphene, MOFs) for enhanced performance. Regeneration is possible for 10–15 cycles, making it one of the most durable polymeric sorbents.

PANI is a conductive polymer with amine (-NH_2) and imine (-N=) functional groups, enabling π-π interactions, hydrogen bonding, and electrostatic interactions with antidepressants. Their characteristics include high surface area, excellent electrical conductivity, porous structural morphology, abundant active sites, mechanical flexibility, and strong chemical stability. It shows wide range linearity such as 0.01–500 ng/mL, with LOD values low as 10 ng/mL. Recovery rates range from 88–99%, and adsorption capacity (~300–450 mg/g) is among the highest for synthetic polymers. PANI's high selectivity and conductivity make it suitable for sensor-based antidepressant detection. However, poor solubility in water, low mechanical stability, and susceptibility to oxidation restrict its long-term application. Regeneration is possible for 8–12 cycles before degradation occurs. PANI-based adsorbents can be efficiently regenerated by adjusting the solution's pH, taking advantage of PANI's reversible doping and dedoping behaviour [152, 153].

Sorption models

The sorption of antidepressant drugs onto sorbent-based materials follows well-defined adsorption models, including Langmuir, Freundlich, and Temkin isotherms, as well as kinetic models such as pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Carbon-based materials (e.g., activated carbon, graphene, carbon nanotubes, and metal-organic frameworks) typically follow the Langmuir model, indicating monolayer adsorption due to π-π stacking, hydrophobic interactions, and electrostatic forces. Previous study reported by Koltsakidou et al. [74] reveal the Langmuir model was the best fit in all operation condition for determining sertraline from aqueous solutions by using graphene oxide.

However, porous materials like activated carbon often fit the Freundlich model, suggesting multilayer adsorption on heterogeneous surfaces. For instance, magnetic adsorbents prepared from carbon-rich aloe vera leaf waste were effectively used for the pre-concentration of selective serotonin reuptake inhibitor (SSRI) antidepressants from aqueous solutions. The adsorption behaviour closely followed the Freundlich isotherm model (R^2 >0.992) and the pseudo-second-order kinetic model (R^2 >0.980), indicating favourable multilayer adsorption and chemisorption processes [68]. Recent study investigated *Xanthium strumarium*-derived activated carbon as a low-cost bioadsorbent, demonstrating a good fit with the Freundlich isotherm model and reporting a maximum

Table 4. Analytical performance of sorbent phase extraction using natural and synthetic polymer-based materials for determining antidepressant drugs

Type	Extraction Mode	Target Analyte	Sample Type	Detection Limit	Recovery	RSD	Reference
Cellulose	SPE	Ami, Imi, Desi, Tri	Biological Fluids	2-3.2[c]	90-121	<8.5	[105]
	FPSE	Ami, Dul, Flu, Vil	Urine	0.38[d]	95-105	<5	[106]
	RPD	Ami, Flu, Ven	Blood, Urine	-	50-98	<10	[107]
	MEPS	Flu	Water, Wastewater	2[d]	76-107	<7	[108]
	FPSE	Ami, Cit, Clo, Flu, Par, Sert, Ven	Blood, Urine, Saliva	0.04-0.06[a]	86-114	<15	[109]
	SPE	Ami, Cit, Imi, Flu, Sert, Ven	Plasma, Urine	-	93-108	<8	[110]
Chitosan	SPE	Desi	Water, Urine	0.39[c]	72-90	<3	[111]
	m-SPE	Ami	Water	37.8[c]	72-90	<4	[112]
	m-SPE	Flu	Urine	5[c]	56-93	2	[113]
	TFME	Flu	Plasma, Urine, Wastewater	0.1-1.6	82-104	<9	[114]
	SPE	Flu	Water, Urine	0.03[c]	96-104	<3	[115]
Polyaniline	SPE	Flu, Nflu	Plasma	-	74-91	<13	[116]
Polydimethylsiloxane	SBSE	Cit, Dulo, Flu, Mir, Par, Sert	Plasma	5-20[d]	38-83	<15	[117]
	SPME	Ami, Clo, Tri	Water	0.079-0.296[c]	82-114	<10	[118]
	SPME	Cit, Flu, Fluv, Sert, Ven	Water	0.015-0.075[d]	88-120	<17	[119]
Poly(methacrylic acid)	SPE	Ami, Clo, Dox, Imi, Nor	Water	0.03-0.12[c]	87-116	<17	[120]
Polypyrrole	MSPE	Flu, Cit	Urine, Wastewater	1.43-1.58[d]	95-106	<5	[12]
	D-μ-SPE	Cit, Sert	Urine, Plasma	0.2-1.0[c]	93-99	<10	[121]
	MEPS	Ami, Cit	Urine	0.03-0.05[c]	88-104	<9	[122]
	SPME	Alp, Imi, Sert	Plasma	0.08-0.27[a]	93-97	<5	[123]
	IT-SPME	Flu, Nflu	Plasma	5[d]	92-110	<13	[124]
	SPME	Imi	Urine, Plasma	0.23-0.45[c]	91-120	<4	[125]
Polystyrene	SS-LPME	Ami, Sert	Wastewater	0.59-2.6[c]	90-100	-	[126]
	D-μ-SPE	Ami, Sert	Water	0.4-0.6[d]	90-98	-	[127]
	μ-SPE	Ami, Cit	Urine	3.1-15[d]	84-119	<15	[128]
Polythiophene	SPME	Cit, Flu, Par, Sert	Plasma	-	76-112	<15	[129]

[a]μg/mL; [b] mg/mL; [c] μg/L; [d]ng/mL; [e] μM; Amit: Amitriptyline hydrochloride; AuNPs: Gold nanoparticles, CD-IMS: Corona Discharge Ion Mobility Spectrometry; Cit: Citalopram; Desi: Desipramine; Esci: Escitalopram; Fe_3O_4: Magnetite nanoparticles; Flu: Fluoxetine; FS: Fluorescent Spectrometry; GC-FID: Gas Chromatography-Flame Ionisation Detector; GC-MS: Gas Chromatography-Mass Spectrometry; HF-SPME: Hallow fibre solid phase microextraction, HPLC: High Performance Liquid Chromatography; HPLC-DAD: High Performance Liquid Chromatography Diode Array Detector; Imip: Imipramine, LC-MS: Liquid Chromatography-Mass Spectrometry; m-d-SPE: magnetic dispersive solid phase extraction; m-SPE: magnetic solid phase extraction; Nort: Nortriptyline; Paro: Paroxetine, PEDOT: Poly(3,4-ethylenedioxythiophene); Sert: Sertaline; SPME: solid phase microextraction; TFME: Thin film microextraction, UV-Vis: Ultraviolet-Visible Light; Ven: Venlafaxine; ZIF: Zeolitic imidazolate framework

adsorption capacity of 64.9 mg/g [154]. Another study by Akpomie and Conradie [155] found that the adsorption of nortriptyline onto silver nanoparticle-loaded, biowaste-derived activated carbon followed the Freundlich isotherm model, with a maximum adsorption capacity of 4.74 mg/g, suggesting a non-uniform distribution of adsorption sites and favourable interaction at lower concentrations.

Kinetic studies show that graphene and CNTs follow pseudo-second-order kinetics, indicating chemisorption, while activated carbon exhibits intraparticle diffusion, where the adsorption rate is influenced by pore structure and drug diffusion. A study conducted by Zhang et al. [156] demonstrated that the pseudo-second-order kinetic model provided the best correlation (R^2) for the adsorption of carbamazepine onto the prepared SPE sorbent, with a maximum adsorption capacity of 25.39 mg/g when applied to plasma samples. A recent study introduced a novel adsorbent, second-generation polyester dendritic-functionalized graphene oxide (PDG-2), for pipette tip micro solid-phase extraction of venlafaxine and desvenlafaxine from urine samples. The PDG-2 sorbent exhibited a rough surface morphology and numerous active functional groups, achieving high adsorption capacities of 230 mg/g for venlafaxine and 187 mg/g for desvenlafaxine. The adsorption process for both analytes followed the pseudo-second-order kinetic model, with excellent correlation coefficients ($R^2 \geq 0.9998$), suggesting a chemisorption-dominated mechanism [157].

Natural polymer-based sorbents, such as cellulose, alginate, chitosan, or natural rubber primarily follow the Freundlich model, as their diverse functional groups (-OH, -COOH, $-NH_2$) provide multiple binding sites for hydrogen bonding, ion exchange, and dipole-dipole interactions. The adsorption isotherm results showed a good fit with the Langmuir model ($R^2 = 0.98$), suggesting that desipramine molecules were evenly distributed across the surface of the βCD-modified chitosan-based magnetic nanocomposite. A previous study demonstrated the successful application of nanomagnetic chitosan/β-cyclodextrin composites for dispersive solid-phase extraction of trace levels of desipramine, highlighting their high selectivity and efficiency in aqueous matrices [111].

However, chemically modified natural polymers, such as cationic alginate beads, may exhibit Langmuir-type adsorption due to strong electrostatic interactions with cationic antidepressants. The adsorption kinetics are typically pseudo-first-order, indicating physisorption-controlled mechanisms, though natural rubber follows pseudo-second-order kinetics due to its hydrophobic interactions with non-polar antidepressants. A previous study reported that alginate extracted from *Bifurcaria bifurcata* was used as a sorbent for the adsorption of venlafaxine and fluoxetine. The adsorption process was more efficient at lower pH levels and followed the Langmuir–Freundlich isotherm model for venlafaxine and the Langmuir model for fluoxetine. Maximum adsorption capacities reached 12 ± 3 μmol/g for venlafaxine and 22 ± 4 μmol/g for fluoxetine in a mono-component system. The difference in adsorption behaviour was attributed to the presence of functional groups with varying polarity in the analyte molecules, which influenced their interactions with the alginate-based adsorbent surface [158]. Barati and co-workers [115] developed a molecularly imprinted polymer based on magnetic chitosan/graphene oxide for the selective separation and preconcentration of fluoxetine from environmental and biological samples. The sorption kinetics followed the pseudo-second-order model with R^2 values close to unity, indicating that the rate-limiting step involves a chemical adsorption process.

Synthetic polymers exhibit varied adsorption behaviours. PS-DVB, PMMA, and PANI fit the Langmuir model, indicating monolayer adsorption driven by hydrophobic and π-π interactions. In contrast, hydrophilic polymers like PVP, PEG, and PAM follow the Freundlich model, as their multiple functional groups allow multilayer adsorption through hydrogen bonding. Conductive polymers such as PPy and PANI often fit the Temkin model, where adsorbate–adsorbent interactions influence adsorption energy.

In a previous study by Bozyiğit et al. [126], polystyrene-coated magnetic nanoparticles (PS@MNP) were used for the adsorption of amitriptyline and sertraline, following the Langmuir isotherm model. The model showed a strong fit for sertraline ($R^2 = 0.9983$) with a high adsorption capacity (20449 μg/g), while amitriptyline showed a weaker fit ($R^2 = 0.9442$) but stronger binding affinity based on K_L values. Both drugs exhibited favourable R_L values, confirming efficient monolayer adsorption on PS@MNP. Contrarily to many studies relying on common isotherm models, Fan et al. [159] found that electrospun polystyrene nanofibers effectively adsorbed olanzapine, risperidone, and clozapine, best fitting the hybrid-type Redlich–Peterson model. Maximum capacities were 12.33, 8.36, and 12.96 mg/g, respectively. The adsorption followed first-order kinetics and was spontaneous, exothermic, and physical, with good reusability over five cycles.

Kinetic studies show that polymers like PPy, PANI, and PS-DVB exhibit pseudo-second-order behaviour, reflecting chemisorptive mechanisms, while PVP and PEG follow pseudo-first-order kinetics, suggesting diffusion-limited physisorption. A study documented

by Khulu et al. [160] utilized a molecularly imprinted polymer (MIP) as an adsorbent for the solid-phase extraction of selected pharmaceuticals, including venlafaxine, from water samples. The adsorption process followed the pseudo-second-order kinetic model, with R^2 values reaching up to 0.9231. This indicated heterogeneity in the binding surface energies of the MIP, leading to multiple interaction mechanisms primarily driven by chemisorption.

Conclusion

Sorbent-phase extraction has gained considerable attention as an effective and versatile approach for the removal and analysis of emerging contaminants, particularly antidepressants, from complex environmental and biological matrices. The extraction performance is significantly improved when sorbent materials are engineered with specific functional groups that enhance selectivity and interaction with target analytes, while the incorporation of retrievable or magnetically responsive features facilitates rapid and efficient recovery post-extraction. In line with the growing emphasis on green analytical chemistry, recent developments have focused not only on eco-friendly material synthesis but also on minimizing solvent use and waste generation throughout the extraction process. Future research is expected to prioritize the design of hybrid extraction systems that integrate multiple techniques to tackle the challenges of selectivity, sensitivity, and matrix complexity. Furthermore, there is a clear shift from single-analyte approaches toward the simultaneous extraction of multiple compounds either within the same therapeutical class or across different drug categories addressing the need for comprehensive monitoring of complex contaminant mixtures in real samples.

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