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REVIEW

Recent Advances of Triazine-Based Materials for Adsorbent Based Extraction Techniques

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Abstract

This review mainly focused on the synthesis and properties of triazine-based materials as well as the state-of-the-art development of these materials in adsorption-based extraction techniques in the past 5 years, such as solid-phase extraction, magnetic solid-phase extraction, solid-phase microextraction and stir bar sorptive extraction, and the detection of various pollutants, including metal ions, drugs, estrogens, nitroaromatics, pesticides, phenols, polycyclic aromatic hydrocarbons and parabens. In the triazine-functionalized composites, triazine-based polymers and covalent triazine frameworks have been developed as the adsorbents with potential for environmental pollutants, mainly relying on the large surface area and the affinity of triazinyl groups with the targets. Triazine-based adsorbents have satisfactory sensitivity and selectivity towards different types of analytes, attributed from various mechanisms including π–π, electrostatics, hydrogen bonds, and hydrophobic and hydrophilic effects. The prospects of the materials for adsorption-based extraction were also presented, which can offer an outlook for the further development and applications.

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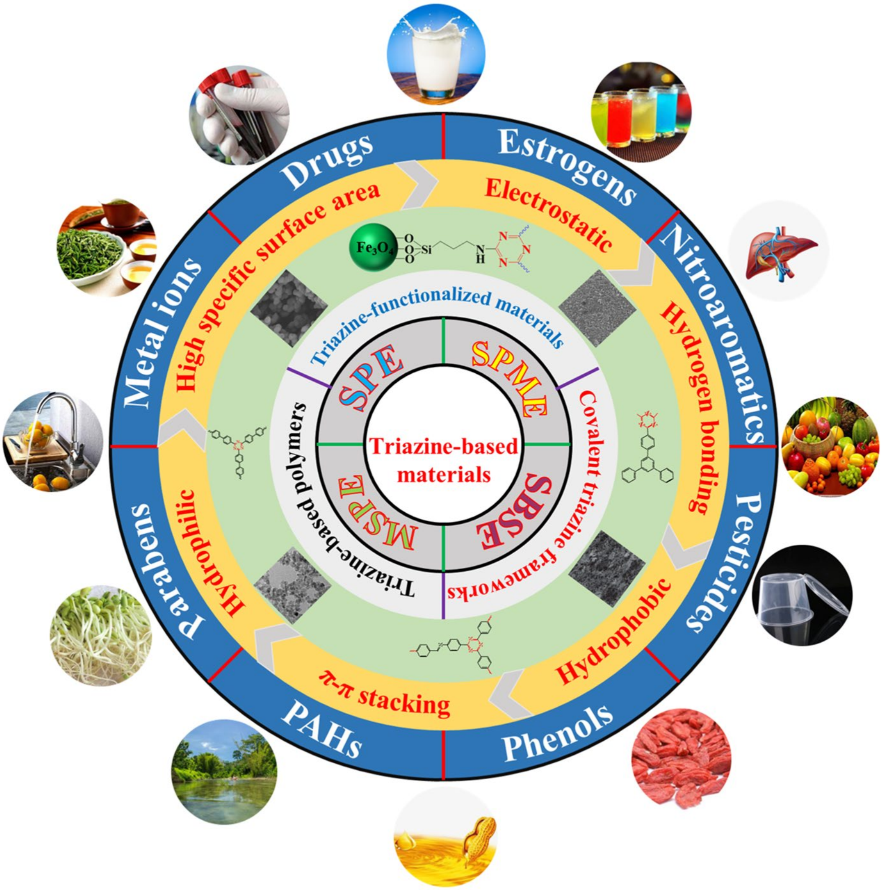
Graphic Abstract



Keywords Triazine-based adsorbent · Solid-phase extraction · Magnetic extraction · Solid-phase microextraction · Stir bar sorptive extraction

Abbreviations

PAHs	Polycyclic aromatic hydrocarbons
SPE	Solid-phase extraction
MSPE	Magnetic solid-phase extraction
SPME	Solid-phase microextraction
SBSE	Stir bar sorptive extraction
LOD	Limit of detection
F_{E}	Enrichment factor
COPs	Covalent organic polymers
COFs	Covalent organic frameworks
CTFs	Covalent triazine frameworks

GO	Graphene oxide
FT-IR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
BET	Brunauer–Emmett–Teller
TEM	Transmission electron microscopy
HPLC	High performance liquid chromatography
XRD	X-ray diffraction
RSDs	Relative standard deviations
UHPLC	Ultra high performance liquid chromatography
DAD	Diode array detector
FLD	Fluorescence detector
β-CD	β-Cyclodextrin
3D	Three dimensional
UV	Ultraviolet
GC	Gas chromatography
FID	Flame ionization detector
PEEK	Polyetheretherketone
PDMS	Polydimethylsiloxane

1 Introduction

Extraction technology is closely related to the development of analytical chemistry, which plays a vital role in obtaining sensitive and accurate results of detection as well as time of analysis. In particular, the detection of trace pollutants has been the focus and difficulty of analytical chemistry. Although these contaminants, like antibiotics [1], heavy metal ions [2], polycyclic aromatic hydrocarbons (PAHs) [3], pesticide residues [4], plasticizers [5], and plant hormones [6], exist at low levels in the sample, they are very toxic, persistent and tend to accumulate in organisms [7]. The presence of trace amounts of contaminants and the complexity of the sample matrix undoubtedly increase the difficulty of sample analysis [8, 9]. Appropriate extraction techniques were selected to eliminate the interference of sample matrix and extract the analytes effectively. Adsorption-based extraction uses a solid adsorbent to enrich or separate the target from the sample matrix and interferences, and then the target is thermally desorbed or eluted by solvent from the adsorbent [10–12]. Compared with solvent-based extraction [13], it has many obvious superior features such as applicability for more types of analytes, less organic solvent, better repeatability, shorter extraction time and facile online combination with analytical instrument [14]. Therefore, it has attracted much more attention recently.

Efficient adsorption-based extraction methods in analytical chemistry mainly contain solid-phase extraction (SPE) [15], magnetic solid-phase extraction (MSPE) [16], solid-phase microextraction (SPME) [17], and stir bar sorptive extraction (SBSE) [18]. These extraction methods are coupled with analytical instruments to accomplish the separation and detection of targets in the sample. Low limit of detection (LOD), large linear range, good correlation coefficient, high enrichment factor

(F_E) and few organic solvents are the main objectives of analytical methods. The type of extraction phase is crucial for the analytical results [19]. Moreover, based on the principle of 'like dissolves like', the extraction phase with the similar property to analytes is often selected [20]. Therefore, the development of extraction materials with high adsorption capacity and good selectivity has become popular for sample preparation. A variety of extraction materials have been researched, such as ionic liquids [21], polymers [22], carbon materials [23], aerogels [24], metal organic frameworks [25], covalent organic frameworks (COFs) [26] and nanomaterials [27].

The triazine-based material has gained popularity in many adsorption materials because of the unique physical and chemical properties [28]. It not only has a high specific surface area but also can provide electrostatics, hydrogen bonding, π–π, and hydrophobic and hydrophilic effects with the various species, so it has been used in chemical sensing, chromatographic analysis, adsorption-based extraction, catalysis and drug controlled release. The triazine-based material can be prepared through the modification of other materials with triazine groups or the polymerization to form triazine-based polymers. In particular, a special polymer called a covalent triazine framework (CTF) [29] is a kind of COF material with good crystallinity, good chemical stability and acceptable thermal resistance, so it has become a hot material in the field of chemistry. Taking into account the importance of adsorption-based extraction and the great potential of triazine-based materials as extraction phases, this review mainly focused on their structure characteristics, preparation methods, characterizations and applications in SPE, MSPE, SPME and SBSE.

2 Preparation and Properties of Triazine-Based Materials

In terms of the diverse chemical composition and structure, triazine-based materials can be divided into three categories: triazine-functionalized composites, triazine-based polymers and CTFs. Because of the differences of their preparation methods and properties, it is necessary to introduce these.

2.1 Triazine-Functionalized Composites

By the functionalization with triazine monomer, the advantage of triazine group can be introduced into the composite and the properties of the composite can be improved. To enhance the dispersion and compatibility of graphene oxide (GO) in epoxy resin, GO was modified by a hydroxyl-terminated triazine derivative. The derivative is constructed from low-cost cyanuric chloride and tris(hydroxymethyl)aminomethane and cyanuric chloride, so abundant hydroxyl and amine groups are introduced, which are capable of curing epoxy resins, then the modified GO intermediate is mixed with an epoxy resin to prepare GO-cyanuric chloride-tris(hydroxymethyl)aminomethane/epoxy composites (in Fig. 1a) [30]. The relationship between surface grafting, chemical construction, morphology, dispersion, and interfacial interaction as well as the corresponding mechanical properties of the composites were studied in detail. The results showed that hydroxyl-terminated

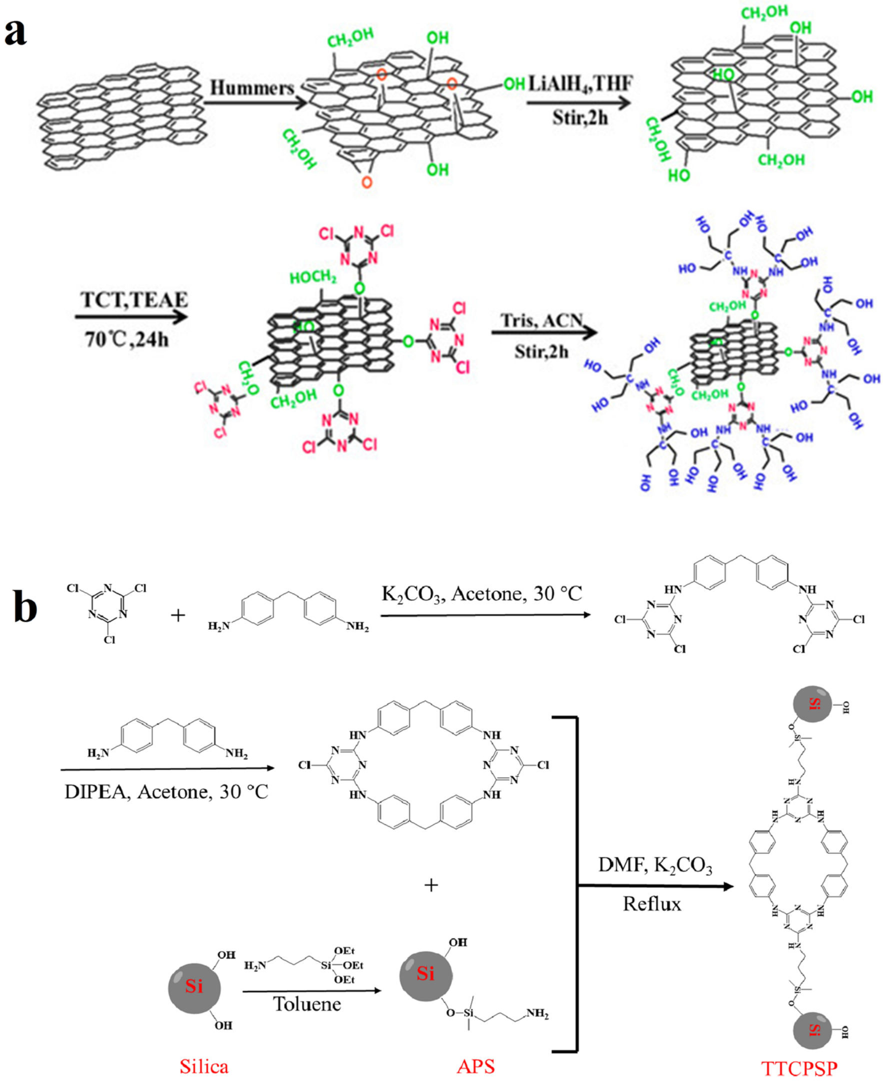


Fig. 1 **a** The route of preparation of graphene oxide-cyanuric chloride-tris(hydroxymethyl)aminomethane [30]; **b** preparation scheme of 1,3,5-triazine tetrad-aza cyclophanes bonded silica gel stationary phase (TTCPSP) [37]

triazine derivative grafted GO contributed to stronger interfacial interaction between GO sheets and the epoxy matrix, which facilitated effective stress transfer from the matrix to the GO-cyanuric chloride-tris(hydroxymethyl)aminomethane sheets. This research indicated that the triazine group could greatly improve the property of the composited material. In the research of Yu’s group, 2,4,6-trichloro-1,3,5-triazine was used as a bridging agent to graft 5′-NH_2-aptamer onto polyhedral oligomeric silsesquioxane-polyethyleneimine affinity monolith, the material was used for the specific identification of ochratoxin A [31]. In comparison with the post-polymerization modification strategies including glutaraldehyde [32, 33] or Au nanoparticles [34, 35] chemically linking reported previously, the reaction efficiency was increased, the modification time was shortened and the properties were improved obviously. Eventually, it was applied to enrich ochratoxin A in beer samples, and acceptable selectivity and sensitivity (0.010 ng mL^{-1}) were obtained. To enhance the hydrophobicity and thermal stability of cellulose nanocrystals, the triazine derivative-grafted cellulose nanocrystals were synthesized via replacing or covering hydroxyl and sulfate ester groups on the surface of cellulose nanocrystals by a triazine derivative, and it was further incorporated into poly(lactic acid) nanocomposites as a reinforcing filler [36]. The grafted cellulose nanocrystals were characterized by contact angle measurement and thermogravimetric analysis (TGA), and satisfactory results with contact angle of 110° and strong thermal stability were obtained, proving the successful modification. Compared to the ungrafted cellulose nanocrystals, improved thermal stability, mechanical properties and good transmittance were achieved. The results confirmed that triazine is an excellent candidate for modifying basis materials to improve their thermal stability and reduce their hydrophilicity. Based on good adsorption and retention of analytes, triazine-functionalized silica materials were also applied to chromatographic stationary phases. Zhang et al. fabricated the 1,3,5-triazine tetrad-aza cyclophanes-functionalized silica (Fig. 1b), that was obtained by stirring a mixture of 1,3,5-triazine tetrad-aza cyclophane, 3-aminopropyl triethoxysilane and *N*,*N*-dimethylformamide at 130 °C for 24 h [37]. The separation performance and retention mechanisms of the stationary phase in high performance liquid chromatography (HPLC) were validated and compared with an octadecylsilyl stationary phase (Agilent ZorBax SB-C18, 5 μm) using different types of compounds including monosubstituted benzenes, PAHs and flavonoids. Due to the hydrophobic, hydrogen bonding and π–π stacking forces provided by the triazine groups, it showed a strong retention for the compounds containing –OH, $-NH_2$ or phenyl groups. These studies suggested that triazine-functionalized composites were endowed with unique advantages or specific functions.

2.2 Triazine-Based Polymers

In the study of controlled release of drugs, in order to avoid the degradation of drugs and accelerate the solubility of drugs in aqueous medium, a novel polybenzimidazole triazine-based polymer was developed by a solvothermal reaction between 4,4′,4″-((1,3,5-triazine-2,4,6-triyl) tris(azanediyl)) tribenzoic acid and 3,3′-diaminobenzidine [38]. Except for high surface area and good thermal stability, the material possessed both electrostatic interactions and π–π stacking forces for drugs, that were necessary for organic carriers. The triazine group has a free electron pair, electron poor character and hydrophilicity, and can act as an active site for interface redox reaction. Dibenzo[b,d]thiophene sulfone is a promising building block for highly efficient organic hydrogen evolution photocatalysts. Based on this, two triazine-conjugated porous polymers were synthesized by Pd-catalyzed coupling 1,3,5-triazine and dibenzo[b,d]thiophene sulfone [39]. These were used as the photocatalysts with excellent solar photocatalytic hydrogen evolution ability. Roshni et al. developed porous covalent triazine piperazine polymer with cyanuric chloride and piperazine as raw materials (in Fig. 2a–d) [40]. Then, mixed matrix membrane prepared with a polymer as filler embedded in poly-ether-block-amide was studied, and it was further applied to the separation of CO_2/N_2 and CO_2/CH_4 gas systems. The porous covalent triazine piperazine polymer was introduced into mixed matrix membranes so that they were rich in nitrogen, which exhibited the better adsorption of CO_2 more than N_2 and CH_4. As a result, the mixed matrix membranes, loaded with covalent triazine piperazine polymer at very low rate, can be significantly improved towards the separation of CO_2/N_2 and CO_2/CH_4 systems in terms of both permeability and selectivity. Recently, Zhao et al. used this method to in situ prepare covalent triazine polymer on SiO_2 (Fig. 2e). The NH_2-SiO_2 was dispersed in anhydrous dichloromethane and mixed evenly with cyanuric chloride at 50 °C for 30 min. Then 1,3,5-triphenylbenzene and $AlCl_3$ were added to the solution and stirred at 50 °C for 16 h to obtain the product [41]. The product was characterized

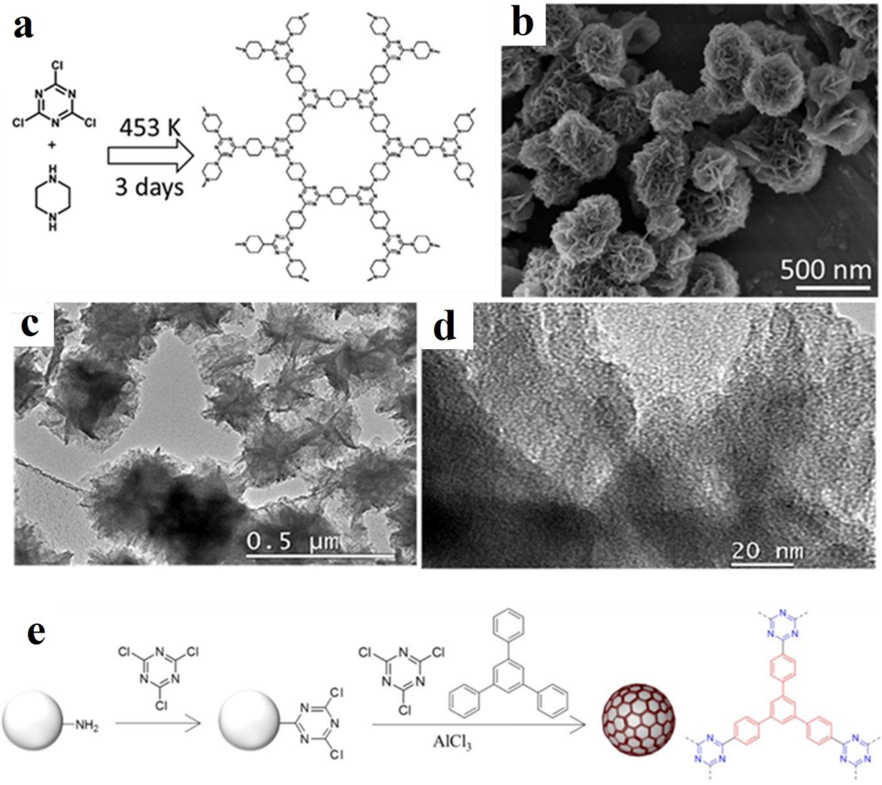


Fig. 2 **a** Schematic illustration of the synthesis and the basic structure of covalent triazine piperazine polymer; **b** SEM image of covalent triazine piperazine polymer powder; **c** TEM image of covalent triazine piperazine polymer powder; **d** high-resolution TEM image focused at the edge of a particle [40]; **e** schematic illustration of the synthetic process of SiO_2@covalent triazine polymer microspheres [41]

by Brunauer–Emmett–Teller (BET), Fourier transform infrared spectroscopy (FT-IR), SEM and transmission electron microscopy (TEM). Monodisperse core–shell microspheres were successfully produced, and the thickness of shells including aromatic units were increased from 70 to 120 and 180 nm by regulating the amount of organic ligands, accompanied by gradually increased surface area from 337 to 381 and 442 $m^2\ g^{-1}$. It was evaluated as HPLC stationary phase and applied to separate various analytes based on hydrophobic, π–π, electron donor–acceptor and hydrogen bonding interactions. This research developed covalent triazine polymer-modified core–shell spheres for chromatographic separation by an in situ method that not only provided an efficient preparation mode but also promoted the widespread applications of covalent triazine polymer.

Ni-catalyzed Yamamoto reaction was also used to synthesize triazine-based covalent organic polymers (COPs). 1,5-Cyclooctadiene was dissolved in a solution of *N*,*N*-dimethyl formamide containing bis(1,5-cyclooctadiene) nickel and 2,2′-bipyridyl, then 2,4,6-tris-(4-bromo-phenyl)-[1,3,5]triazine was added to the above mixture and the reaction was performed at 105 °C under N_2 overnight [42]. The COPs displayed graphene-like layer texture, good thermal stability, very high surface area (2015 $m^2\ g^{-1}$) and evenly distributed pore volume (1.36 $cm^3\ g^{-1}$). Disordered porous structural nature revealed by X-ray diffraction (XRD) patterns may be because of the distortion of the benzene ring or the interpenetration of the monomers.

Aerogels are a special class of nano-porous materials, and they are a microporous solid gel with a gaseous dispersion phase, approximately 95% of the volume is air and the remaining 5% is solid, making it the lightest solid material in the world. They have unique properties such as extremely low density (0.003–0.5 $g\ cm^{-3}$), high porosity and ultra-high specific surface area (500–1500 $m^2\ g^{-1}$); therefore, they exhibit excellent potential for extraction and adsorption. Some triazine-based organic polymers were developed as the organic aerogels, which were prepared through Schiff–Base reaction between melamine and formaldehyde under certain conditions [43].

2.3 Covalent Triazine Frameworks

CTFs are one special triazine-based polymer, their interior is a porous framework material formed via connecting organic functional groups with the triazinyl [44]. The covalent bonds give them good chemical stability and thermal resistance. CTFs combining the advantage of triazine-based polymers and a highly ordered pore structure are considered one class of excellent adsorption and extraction material. As shown in Fig. 3, there are various methods to synthesize CTFs.

Among many preparation methods, the trimerization reaction catalyzed by $ZnCl_2$ and CF_3SO_3H is the most common method for the synthesis of CTFs. $ZnCl_2$ had good solubility in nitrile reactant, and also gave high catalytic activity to trimerization. Kuhn et al. used 1,4-dicyanobenzene as reagent and $ZnCl_2$ as catalyst to synthesize CTF material at 400 °C. Products prepared under different temperatures and reaction times were characterized by elemental analysis and FT-IR. After the reaction at 400 °C for 40 h, the product was of high purity and the reaction was

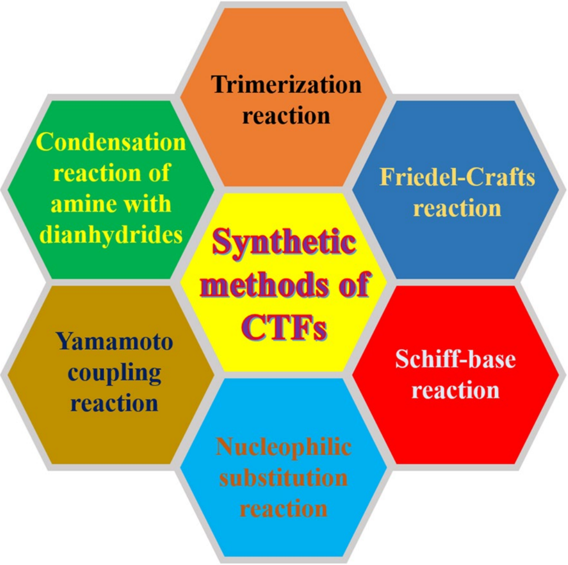


Fig. 3 The synthetic methods of CTFs

carried out more thoroughly [45]. Similarly, benzimidazole was used to synthesize benzimidazole-linked CTF by Tao et al. [46]. They found that the porosity increased with the raise of $ZnCl_2$ concentration, but CTF changed to amorphous form with high concentration of catalyst. In this work, the benzimidazolium-based CTF with high surface area (1549 m^2 g^{-1}) was used to adsorb CO_2 and high uptake capacity reached 21.68 wt%. A series of CTFs were synthesized at room temperature under trifluoromethanesulfonic acid as catalyst and microwave assisted conditions [47]. The CTFs were characterized by FT-IR, the results were basically consistent with those obtained by ionothermal $ZnCl_2$ catalysis, but the reaction time was greatly compressed. TGA investigation exhibited good thermal stability of CTFs at 600 °C. The high thermal, chemical and mechanical stability and the formability of a thermoset polymer material from CTFs, give them broad application prospects in gas storage and sensors.

It is different from the high reaction temperature required by trimerization reaction, the Friedel–Crafts alkylation reaction only required mild conditions and also was widely used in the synthesis of CTFs from aromatic hydrocarbons and haloalkane. Soltani et al. reported the use of the CTF-grafted mesoporous silica materials as a novel adsorbent for the assessment of its capability for organic dyes removal from aqueous solution [48]. Cyanuric chloride and biphenyls were added to Ph-SBA-15 and uniformly dispersed in dichloromethane in Ar (0 °C) until fully dissolved, followed by adding anhydrous $AlCl_3$ catalyst, and the reaction mixture was refluxed at 65 °C under Ar atmosphere and moderate stirring for 16 h. After washing and drying, the material was obtained and investigated for the adsorption of methylene blue, and the effects of sample pH, the initial concentration of methylene blue, contact time, adsorbent dosage, and temperature were systematically tested. Because there were a large number of aromatic groups on the adsorbent, the hydrogen bonding and π–π stacking forces between the adsorbent and methylene blue resulted in high removal efficiency (569 mg g^{-1}) under the optimum conditions (in Fig. 4).

Triazine monomers with amino groups are well suited for the preparation of CTFs by Schiff-Base reaction. Xu et al. developed two CTFs through reacting 2,4,6-tris(4-aminophenoxy)-1,3,5-triazine with 2,4,6-tris-(4-formylphenoxy)-1,3,5-triazine or terephthalic aldehyde, respectively (in Fig. 5), the characterizations of FT-IR, X-ray diffraction (XRD) and BET proved very good crystallinity and high specific surface area (1589 m^2 g^{-1} and 1441 m^2 g^{-1}) for two CTFs [49]. As shown in Fig. 6a, He et al. synthesized novel C_3N_4 active center inlaid CTFs by Schiff-Base reaction between 1,3,5-triformylphloroglucinol and melamine [50]. As can be observed by SEM and TEM, the material shows the thread-like morphology and width of 60–180 nm in Fig. 6b, c. The prepared material had good chemical durability to water, acids and bases, and exhibited superior visible light photocatalytic ability for the removal of organic contaminant. It provides a feasible approach towards the design and construction of highly efficient visible-light-induced photocatalysts with desired band structures.

The preparation of CTFs by nucleophilic substitution reaction has attracted more and more attention. As shown in Fig. 7a, cyanuric chloride and 1,4-phenylenediamine were reacted in 1,4-dioxane with the presence of anhydrous K_2CO_3 at 90 °C for 3 days [51], the developed CTF was successfully applied in the field of electrochemistry. This method was used more and more frequently in recent years because of its controllable conditions.

Wang et al. synthesized two CTFs by stable condensation of amine (melamine) with dianhydrides (pyromellitic dianhydride and naphthalene tetracarboxylic dianhydride) [52]. In this work, two reactants with the molar ratio of 1:1 were mixed and heated to 325 °C by N_2 shield, the solids were ground and washed to get the final products (in Fig. 7b). However, this method for synthesizing CTFs is not common in practical applications.

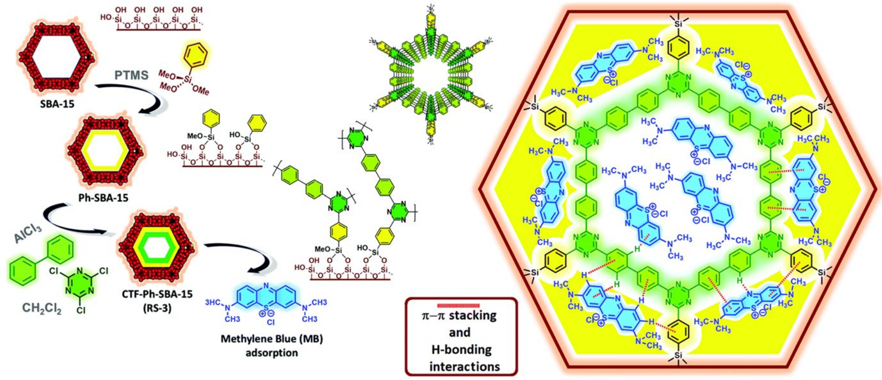


Fig. 4 Schematic representation of the overall synthesis strategy of the CTF-Ph-SBA-15 (RS-3) and the adsorption of methylene blue (MB) onto the RS-3. The π–π and H-bonding, the proposed schematic interactions, between adsorbate and the surface of the adsorbent are also shown (red dashed lines) [48]

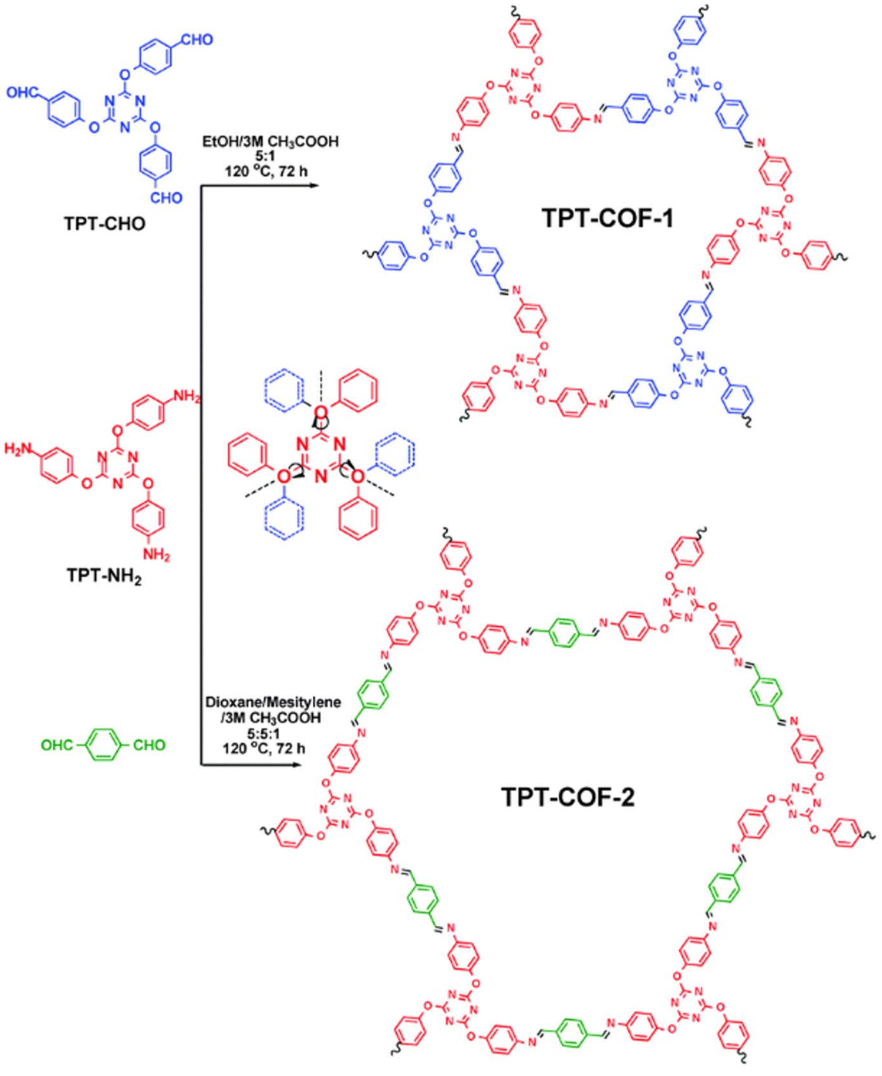


Fig. 5 The synthetic route to TPT-COFs [49]

In addition to the above reaction types, other preparation methods were also explored. For example, Wang et al. developed a method by Michael addition and Schiff-Base reaction [53]. Four different CTFs were prepared by this condensation method in this work. Taking dimethyl sulfoxide as the solvent, Cs_2CO_3 as the substrate, 4,4′-biphenyl-dialdehyde and tris(4-formylphenyl)-amine as the reactants in a sealed container at 120 °C, the CTF product was obtained. The composited preparation method was introduced into the synthesis of CTF, providing a new idea for the preparation of CTF.

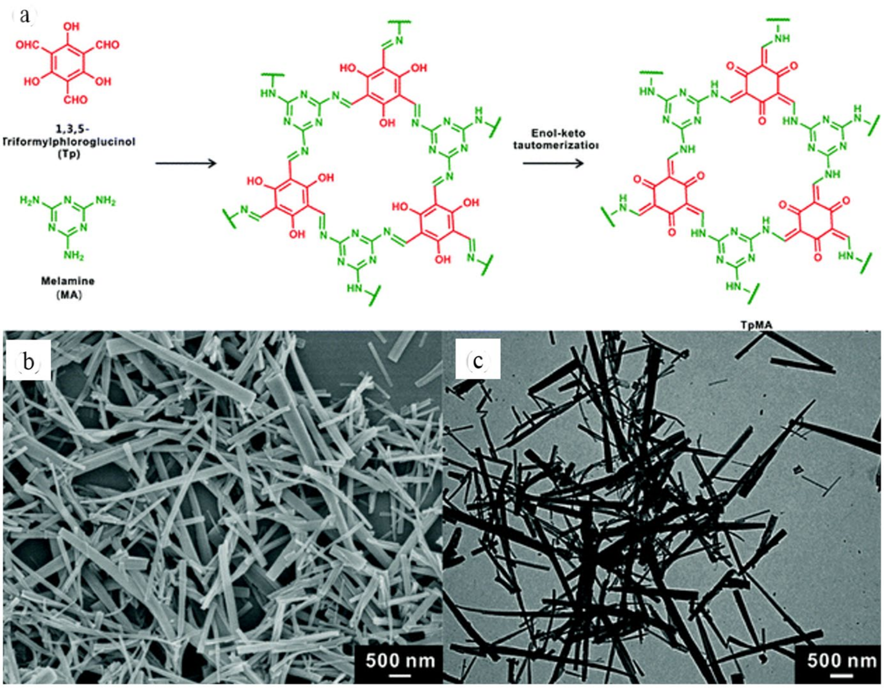


Fig. 6 **a** Schiff-Base reaction followed by irreversible enol-to-keto tautomerization of CTF; **b** SEM image; **c** TEM image [50]

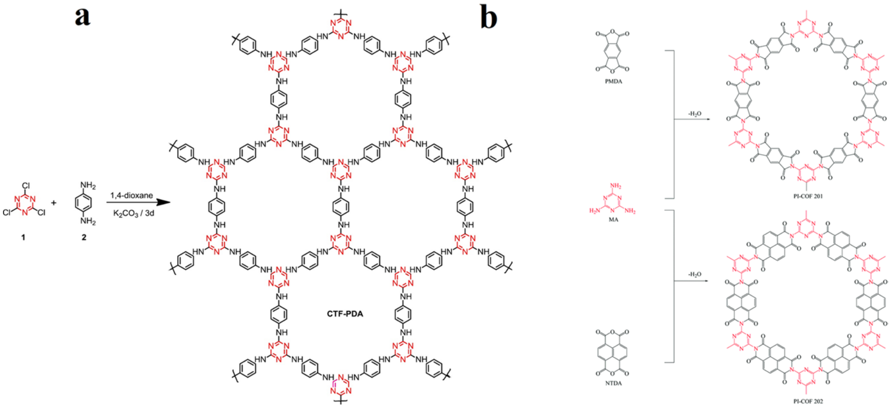


Fig. 7 **a** Synthesis of CTF-PDA [51]; **b** schematic representation of the synthesis processes of PI-COF 201 and PI-COF 202 [52]

In a word, it is believed that CTFs with better performance and simpler preparation methods will be further developed by researchers in the near future.

3 Adsorbent Based Extraction Techniques

3.1 Solid-Phase Extraction

SPE is a common sample pretreatment technique, which separates the target from other interferences by selective adsorption onto the solid phase. The solid phase is the extraction material or adsorbent that decides the extraction efficiency. The triazine-based materials are widely applied as the adsorbents for SPE due to the excellent adsorption performance (see Table 1).

3.1.1 Triazine-Functionalized Silica as Adsorbents

In recent years, triazine-functionalized silica materials developed by bonding triazinyl groups with silica matrix were increasingly used for SPE. As shown in Fig. 8a, 3-chloropropyltrimethoxysilane was used as the bridging agent to bond 2,6-diamino-4-phenil-1,3,5-triazine to the surface of silica for SPE of Se(IV) ions from food samples [54]. The established method was applied to the analysis of fish, egg, honey, corn flour and rice flour with stable experimental data (relative standard deviations, RSD, $<8\%$) and high recovery more than 95%. Because the adsorption mechanisms are different for organic compounds and metal ions, it is very rare to use SPE to concentrate two classes of targets simultaneously. Through the hydrophobic effect and π–π stacking between triazinyl and phenyl of organic compounds, and the chelating interaction of triazine units with Cu(II), tetraazacalix[2]arene[2]triazine-modified silica as a SPE adsorbent [55] determined five PAHs and Cu(II) by HPLC and graphite furnace atomic absorption spectroscopy, respectively. The main extraction and desorption conditions were optimized, and the analytical method was established with low LODs (0.4 ng L^{-1} for PAHs, 15.0 ng L^{-1} for Cu(II)), wide linear ranges (0.25–100 ng L^{-1} for PAHs, 0.10–100 μg L^{-1} for Cu(II)) and low RSDs ($<6.4\%$). The material has also been used for the extraction and detection of flavonoids in complex food samples [56]. The pH of sample solution, sample flow rate, composition and volume of eluent solvent were optimized to establish analytical method. The analysis of quercetin, luteolin and kaempferol in grape juice sample was carried out by ultrahigh performance liquid chromatography-diode array detector (UHPLC-DAD), which had lower LOD (50 μg L^{-1}) and higher recovery than that in commercial C18. The group also used it to enrich benzo[α]pyrene in edible oil [57]. Using SPE-HPLC-fluorescence detector (FLD) method, the overall recovery of 88.0–122.3%, the LOD of 0.03 μg kg^{-1}, and RSDs lower than 9.2% were obtained. Another similar material was also prepared to analyze biological samples. A bis(tetraoxacalix[2]arene[2]triazine)-modified silica (in Fig. 8b) was synthesized as the sorbent for the extraction of five anthraquinones from human urine by hydrophobic, hydrogen bonding, and π–π stacking mechanism [58].

Table 1 The recent applications of triazine-based adsorbents for solid-phase extraction

Adsorbents	Analytes	LODs (μg L^{-1})	Linear ranges (μg L^{-1})	Samples	Detection methods	Ref
2,6-Diamino-4-phenil-1,3,5-triazine bonded silica	Se(IV)	0.015	–	Water and food samples	Graphite furnace atomic absorption spectrometry	[54]
Tetraazacalix[2]arene[2]triazine bonded silica	Five PAHs and Cu(II)	0.0004 PAHs, 0.015 Cu(II)	0.0005–0.1 PAHs, 0.1–100 Cu(II)	River water samples	HPLC-fluorometric detection (PAHs), graphite furnace atomic absorption spectrometry (Cu(II))	[55]
Bis(tetraoxacalix[2]arene[2]triazine)-modified silica	Three flavonoids	0.5	5.0–200	Grape juice	UHPLC-DAD	[56]
Tetraoxocalix[2]arene[2]triazine bonded silica	Benzo[α]pyrene	0.03 μg kg^{-1}	0.1–100 μg kg^{-1}	Edible oils	HPLC-FLD	[57]
Bis(tetraoxacalix[2]arene[2]triazine) modified silica	Five anthraquinones	3.9	12.0–1800	Human urine	UHPLC-FLD	[58]
Mesoporous melamine–formaldehyde polymer	Sialylated glycopeptides	–	–	HeLa S3 cell lysate sample	Hydrophilic interaction liquid chromatography-MS	[60]
Molecularly imprinted melamine-urea–formaldehyde monolithic resin	Three plant growth regulators	0.001 μg g^{-1}	0.03–5.00 μg g^{-1}	Bean sprouts	HPLC–UV	[61]
Molecularly imprinted phloroglucinole-formaldehydee-melamine resin	Clorprenaline and bambuterol	3.9	15.0–3000	Urine	HPLC–UV	[62]
β-Cyclodextrin-modified three-dimensional graphene oxide wrapped melamine foam	Three flavonoids	0.5	5.0–200	Lycium barbarum	HPLC–UV	[63]

Table 1 (continued)

Adsorbents	Analytes	LODs (μg L^{-1})	Linear ranges (μg L^{-1})	Samples	Detection methods	Ref
Phenylboronic acid modified hybrid material composed of graphene oxide and melamine sponge	Five nucleosides	1.0	3.0–5000	HepG2 cells	HPLC–UV	[64]
Melamine sponge functionalized with urea–formaldehyde *co*-oligomers	Ten hydrophobic analytes	0.01	1.0–100	Lake water	HPLC–DAD	[65]
Melamine sponge decorated with copper sheets	Ten sulfonamides	0.008	0.5–150	Lake water and milk	HPLC–DAD	[66]
Melamine-based porous organic polymers	Five phytohormones	0.04	0.5–100	Two juice	HPLC–UV	[67]
Covalent triazine framework-1	Three nitroimidazoles	0.11	0.5–500	Porcine liver and waters	HPLC–UV	[68]

Water and food samples: drinking water from Tokat city, mineral water from the market, soda water, tap water from Tokat city, veal liver, tuna fish, canned fish, egg, corn flour, rice flour, wheat flour, broad bean, hazelnut, garlic, broccoli, spinach, leek, pumpkin, cabbage; five PAHs: phenanthrene, anthracene, triphenylene, chrysene, perylene; three flavonoids: quercetin, luteolin, kaempferol; five anthraquinones: aloe-EMODIN, emodin, physcion, chrysophanol and rhein; three plant growth regulators: 1-naphthaleneacetic acid, 2,4-dichlorophenoxyacetic acid, *p*-chlorophenoxyacetic acid; three flavonoids: quercetin, quercetin-3-o-rhamnoside, rutin; five nucleosides: cytidine, uridine, inosine, guanosine, adenosine; five phytohormones: salicylic acid, indole-3-acetic acid, abscisic acid, 1-naphthaleneacetic acid, 2,4-dichlorophenoxyacetic acid; two juice: tomato juice, grape juice; three nitroimidazoles: metronidazole, ronidazole and dimetridazole; ten hydrophobic analytes: fenbufen, butylparaben, benzophenone-8, cumylphenol, flurbiprofen, chlorpyrifos, trifluralin, 4-octylphenol, tonalide, deltamethrin

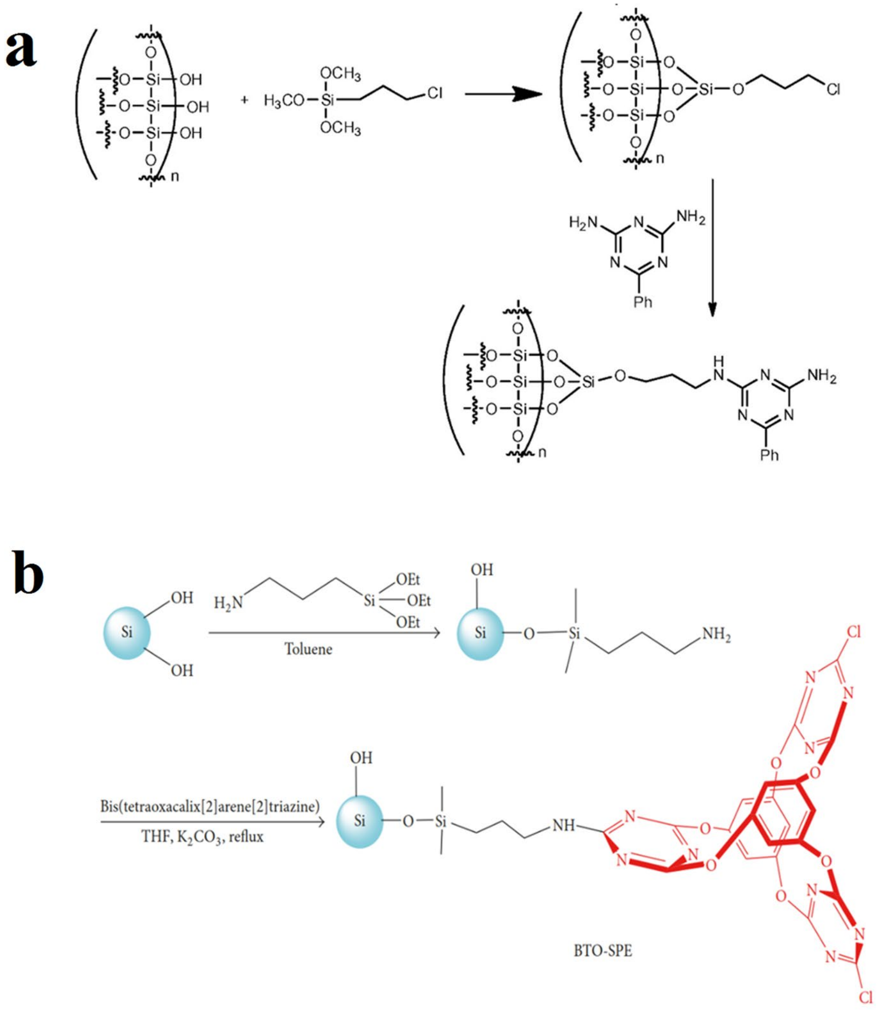


Fig. 8 **a** Synthesis of 2,6-diamino-4-phenil-1,3,5-triazine bonded silica [54]; **b** preparation scheme of bis(tetraoxacalix[2]arene[2]triazine)-modified silica SPE sorbent [58]

Coupled with UHPLC-FLD, the developed method with LODs ranged from 3.9 to 5.7 ng mL^{-1} was successfully applied to the determination of aloe-emodin, rhein, emodin, chrysophanol and physcion in the urine samples of five patients. Another new triazine-containing silica adsorbent (2,6-bis(5,6-dioctyl-1,2,4-triazine-3-yl)pyridine@SiO_2) was produced by the similar method [59]. In the presence of Sr(II), Pd(II), Li(I), Na(I), Cs(I), K(I), Rb(I) and Ba(II) in nitric acid solution, it selectively removed Pd(II) with the removal efficiency more than 99.2%, that proved a good application prospect in adsorption of Pd(II).

3.1.2 Triazine-Based Polymers as Adsorbents

It is known that the extraction of hydrophilic targets is very difficult in sample preparation. However, most small molecules in organisms are hydrophilic, so their rapid and accurate detection from biological samples is an urgent problem. A hydrophilic SPE method based on mesoporous melamine–formaldehyde polymer was developed, followed by nano-ESI–Q/TOF MS analysis [60]. In the extraction of sialylated glycopeptides from biological samples, the material exhibited hydrophilic and positively charged surface under low pH conditions. Due to the synergistic effect of hydrophilic and electrostatic interactions, the targets were well retained on the material. The method presented acceptable recovery of 75.63% from tryptic of HeLa S3 cell lysate sample.

The introduction of a molecular imprinting technique can effectively improve the selectivity of SPE to specific targets. Using dopamine hydrochloride as template, and melamine, urea and formaldehyde as reactants, Qiao et al. synthesized a hydrophilic molecularly imprinted monolithic resin [61]. It was attached to a pipette head for SPE of 1-naphthaleneacetic acid, *p*-chlorophenoxyacetic acid and 2,4-dichlorophenoxyacetic acid from bean sprouts (in Fig. 9a). The ratio among melamine, urea and formaldehyde was optimized to get high selectivity of the material, the recognition mechanism mainly included hydrophilic effect and π–π stacking. After optimizing the extraction and desorption conditions, the pipette tip-SPE method was successfully applied to the detection of above plant growth regulators in bean sprouts. Another molecularly imprinted phloroglucinol-formaldehyde-melamine resin (in Fig. 9b) was developed to detect clorprenaline and bambuterol in urine [62]. The preparation conditions were explored using phenylephrine as template molecule, and the proportions of melamine, phloroglucinol and formaldehyde were optimized. SEM observed that the rough morphology of the material was very consistent with three dimensional (3D) network structure. BET investigated a much higher surface area of material (228.9 $m^2\ g^{-1}$) than non-imprinted resin (7.8 $m^2\ g^{-1}$). Compared with strong cation-exchange adsorbent, C18 and non-imprinted material, the

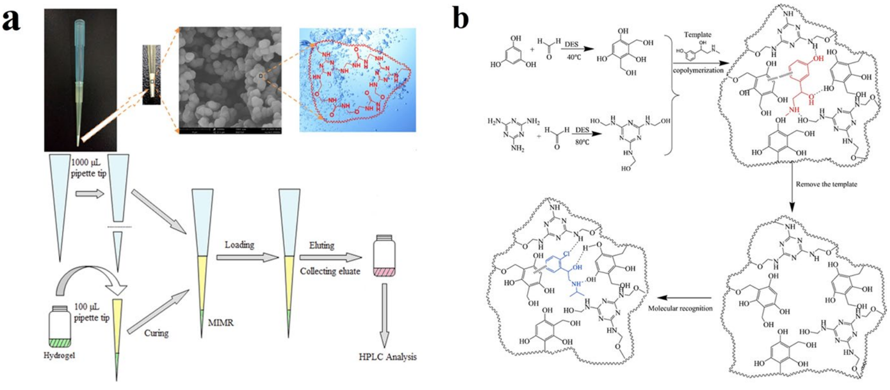


Fig. 9 **a** Procedure of pipette tip-solid-phase extraction [61]; **b** schematic illustration of synthesis and molecular recognition of molecularly imprinted phloroglucinol-formaldehyde-melamine resin [62]

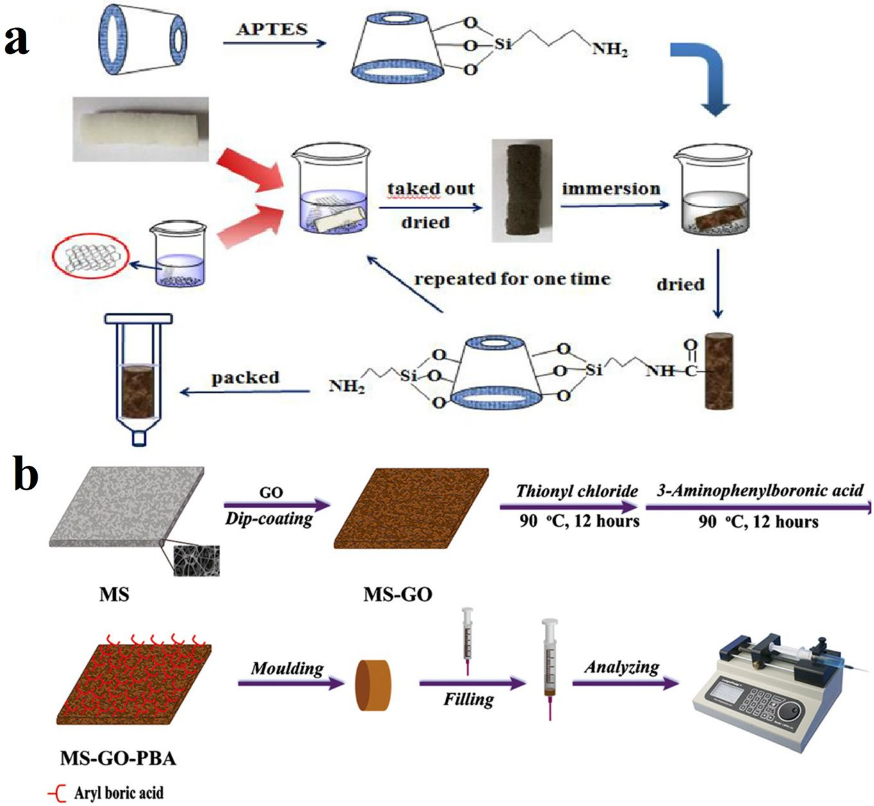


Fig. 10 **a** Schematic illustration of the preparation process of the 3D β-cyclodextrin/GO-wrapped melamine foam [63]; **b** schematic for the preparation of boronic acid modified grapheme oxide/melamine sponge composite for in-syringe solid-phase extraction [64]

imprinted material had the highest recovery (91.7–100.1%) for clorprenaline and bambuterol.

Commercial melamine foam is a green, inexpensive, highly porous triazine-based polymer material that can be selected as a substrate to fabricate the sorbent with other functional components. As shown in Fig. 10a, Hou et al. has modified GO and β-cyclodextrin (β-CD) onto the surface of melamine foam to get a 3D β-CD/GO-wrapped melamine foam via a layer-by-layer assembly for the extraction of flavonoids [63]. The introduction of melamine foam prevented the accumulation of GO sheets and greatly increased the utilization of its surface area. Further, the results indicated that β-CD improved the extraction selectivity due to the formation of β-CD-flavonoid inclusion complexes through the host–guest interaction. In this work, the SPE-HPLC method exhibited the linear range of 5.0–200 μg L^{-1} for quercetin, 2.0–200 μg L^{-1} for rutin and quercetin-3-*O*-rhamnoside with LODs of 0.5–2.0 μg L^{-1}. The phenylboronic acid and GO were also used to modify melamine sponge for developing the adsorbent of nucleosides (cytidine, uridine, inosine, guanosine and adenosine) [64]. The material was made into a column that was loaded into a syringe, and semi-automated SPE was performed by a peristaltic pump (in Fig. 10b). By advantage of boron affinity, the material provided good extraction selectivity and enrichment ability to the targets. The method realized the detection of five nucleosides from HepG2 cells, but the service life was only six times, so the material performance in this respect still needed to be improved. In order to improve the hydrophobicity of the melamine sponge, its surface was modified with urea–formaldehyde *co*-oligomers [65]. The functionalized material was used to extract ten hydrophobic analytes. By optimizing sample volume, sample pH, ionic strength and desorption solvent volume, a highly selective and sensitive SPE-HPLC–DAD method was established, getting low LOD (0.03 μg L^{-1}), large linear range (1.0–100 μg L^{-1}) and satisfactory recoveries (92–100%). Based on the good results of the melamine sponge in the above tests, functionalizing it with copper sheets was considered. Since copper has excellent affinity for sulfonamides, sulfonamides were selected as the targets. The melamine sponge with metallic copper sheets was directly immersed in the sample solution and sulfonamides from lake water and milk samples was quantified by HPLC [66]. This method had the merits of wide linearity, low limits of quantification (LOQs) (0.025–0.057 μg L^{-1} for lake water, 0.23–1.05 μg L^{-1} for milk), high F_E (25–41) and satisfactory recovery and repeatability.

Furthermore, melamine-based porous organic polymers was designed for online SPE through a cross-linking reaction between melamine and paraformaldehyde [67]. It provided good extraction capacity and high adsorption efficiency for phytohormones in juice samples, attributed to the π–π and hydrogen bond effect by the rich π-electron and *N*-containing triazine structure of sorbent. The online SPE-HPLC–UV method successfully analyzed trace five phytohormones from tomato and grape juice samples, with the relative recovery ranging in 83.1–116% and 87.2–121%, respectively.

3.1.3 Covalent Triazine Frameworks as Adsorbents

For the highly selective extraction of nitroimidazoles, 1,4-dicyanobenzene was used as the reactant and $ZnCl_2$ as the catalyst to synthesize CTF-1 by a simple trimerization at 400 °C. The material of 20 mg was filled into a micro-column, and two columns were attached in parallel to an eight-way valve for online SPE before HPLC-ultraviolet (UV) analysis. After optimizing sample volume, sample flow rate, ionic strength and desorption conditions, online SPE-HPLC–UV method was established for three nitroimidazoles in environmental water and porcine liver samples. Owing to the π–π interaction and hydrogen bonding between CTF-1 and nitroimidazoles, the online method provided lower LODs of three nitroimidazoles than other extraction methods prior to HPLC–UV detection, and it also avoided possible contamination and loss of sample, enhanced the sample throughput to seven tests each hour [68].

3.2 Magnetic Solid-Phase Extraction (MSPE)

Magnetic absorbents have exhibited great potential for the rapid and efficient removal of trace pollutants from water or oil separation in water by magnetic reusability [69, 70], and they also have been developed and widely used in the field of SPE. Compared with traditional SPE, MSPE has the advantages of simple operation, rapid extraction, less amount of organic solvent, easy recovery of extraction material and good repeatability. The triazine-based materials displayed good properties in MSPE (see Table 2).

3.2.1 Triazine-Functionalized Magnetic Nanoparticles as Adsorbents

For rapid and highly sensitive detection of Pb(II) and Cd(II) ions in the environment, a triazine-based material was developed for MSPE. Ghanbari et al. used 2,4-bis(3,5-dimethylpyrazol)-triazine and *N*-ethyldiisopropylamine to synthesize 3-aminopropyltriethoxysilane-2,4-bis(3,5-dimethylpyrazol)-triazine in N_2 at 80 °C. It was modified to SiO_2-coated Fe_3O_4 using 3-aminopropyltriethoxysilane as a bridging agent. The material with high surface area of 402 $m^2\ g^{-1}$ was used as an adsorbent in MSPE, and Pb(II) and Cd(II) ions were quantitatively detected by atomic absorption spectroscopy. The effect of pH, extraction time, type of eluent, eluent volume, eluent time and interfering ions was separately investigated. The established method gave LODs for Pb(II) (0.7 ng mL^{-1}) and Cd(II) (0.01 ng mL^{-1}), and it was applied to the quality inspection of various fruits with satisfactory results [71]. Similarly, this group also used the material for the extraction of Cr(VI) by MSPE [72]. The method was validated by certified reference material (SRM 2109 Cr(VI) standard solution), the analytical results were in good agreement with the real results. In the real sample analysis, the test results were also satisfactory. Compared with some MSPE methods based on other materials, there were some advantages in LOD, adsorption capacity and repeatability. These works provided new ideas for the use of triazine-based materials in MSPE. As mentioned above, the tetraazacalix[2]arene[2]triazine@SiO_2 was used as a SPE adsorbent for Cu(II) and PAHs [55]. However, MSPE has significant advantages over SPE, so this group prepared tetraazacalix[2]arence[2]triazine-coated Fe_3O_4/SiO_2 magnetic nanoparticles to extract five PAHs, six nitroaromatics and four metal ions by MSPE [73]. Compared to previous work, the material showed lower LODs for PAHs, which may be caused by more adequate contact between nanoparticles sorbent and targets.

3.2.2 Triazine-Based Polymers as Adsorbents

Adsorption-based extraction is increasingly used for drug detection. Melamine–formaldehyde resin was synthesized on the surface of Fe_3O_4 nanoparticles by water-in-oil method for the extraction of drug. The enrichment and detection of nine nonsteroidal anti-inflammatory drugs in urine and milk samples were realized via MSPE-HPLC–UV. High specific surface area, good dispersion, and strong intermolecular forces of the material with the analytes achieved satisfactory recoveries (80.6–116.3%), low LODs (0.3–1.5 μg L^{-1}) and acceptable RSDs (3.0–11.4%)

Table 2 The recent applications of triazine-based adsorbents for magnetic solid-phase extraction

Adsorbents	Analytes	LODs (μg L^{-1})	Linear ranges (μg L^{-1})	Samples	Detection methods	Ref
Triazine-modified magnetite nanoparticles	Pb(II), Cd(II)	0.7	3.0–100	Fruit samples	Flame atomic absorption spectrometry	[71]
Triazine-modified Fe_3O_4 nanoparticles	Cr(VI)	2.0	–	Tap water	UV–Vis	[72]
Tetraazacalix[2]arence[2] triazine coated Fe_3O_4/SiO_2	Five PAHs	0.00009	0.0005–0.05	Urine	HPLC-FLD	[73]
	Six nitroaromatics	0.006	0.02–0.2	Surface and ground waters	HPLC–UV	
	Metal ions	0.017	0.02–2.0	Surface and ground waters	Atomic absorption spectrometry	
Magnetic melamine–formaldehyde resin	Nonsteroidal anti-inflammatory drugs	0.2	1.0–5000	Urine and milk samples	HPLC–UV	[74]
Triazine-imine core–shell magnetic covalent organic polymer	Eight pesticides	0.0004	0.005–5.0	Fruit samples	UHPLC-MS/MS	[75]
Triazine-based polymeric modified Fe_3O_4/GO	Acidic and basic pesticides	0.17	5.0–500	Water and food samples	HPLC–UV	[76]
Magnetic porous covalent triazine-based organic polymer	Five carbamate pesticides	0.02	0.9–80.0	Juice samples	HPLC–MS	[77]

Table 2 continued

Adsorbents	Analytes	LODs (μg L^{-1})	Linear ranges (μg L^{-1})	Samples	Detection methods	Ref
Magnetic covalent triazine-based frameworks	Six perfluorinated compounds	0.00062	0.005–4.0	Water samples	HPLC–MS/MS	[78]
Covalent triazine-based frameworks/iron oxide	Seven phenolic pollutants	0.09	25–2000	Water samples	HPLC-UVD	[79]
Covalent triazine-based framework	Four parabens	0.02	0.1–500	Multiple real samples	HPLC–UV	[80]
Magnetic covalent triazine framework	Six phthalate esters	0.15	2.0–100	Plastic packaging	GC-FID	[81]

Fruit samples: citrus leaves, orchard leaves; five PAHs: phenanthrene, anthracene, pyrene, chrysene, and benzo(a)pyrene; Six nitroaromatics: 4-nitrotoluene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, 4-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol; four metal ions: Cu, Zn, Mn, Cd; nonsteroidal anti-inflammatory: indoprofen, naproxen, ketoprofen, carprofen, indometacin, flufenamic acid, mefenamic acid, tolfenamic acid; eight pesticides: diflufenican, picoxystrobin, quinoxyfen, furametpyr, fenhexamid, benalaxyl, carbendazim, penconazole; fruit samples: strawberry and grape samples; acidic and basic pesticides: Imidacloprid and 2,4-dichlorophenoxyacetic acid; water and food samples: cucumber, tomato and tap water; five carbamate pesticides: propoxur, carbaryl, isoprocarb, fenobcarb and diethofencarb; juice samples: lemonade and grape juice samples; six perfluorinated acid compounds: perfluorobutyric acid, perfluoropentanoicacid, perfluoroheptanoic acid, perfluorooctanoic acid, perfluorononanoicacid, perfluorodecanoic acid; seven phenolic pollutants: phenol, 4-nitrophenol, 2-nitrophenol, 2-chlorophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol; water samples: tap water, spring water, and pond water samples; four parabens: methylparaben, ethylparaben, propylparaben, butylparaben; multiple real samples: human urine, breast milk, personal care products, and shower wastewater; six phthalate esters: dimethyl phthalate, diethyl phthalate, di-*n*-butyl phthalate, ben-zyl butyl phthalate, di-2-ethylhexl phthalate, and di-*n*-octyl phthalate; plastic packaging: disposable plastic cup and mineral water bottle

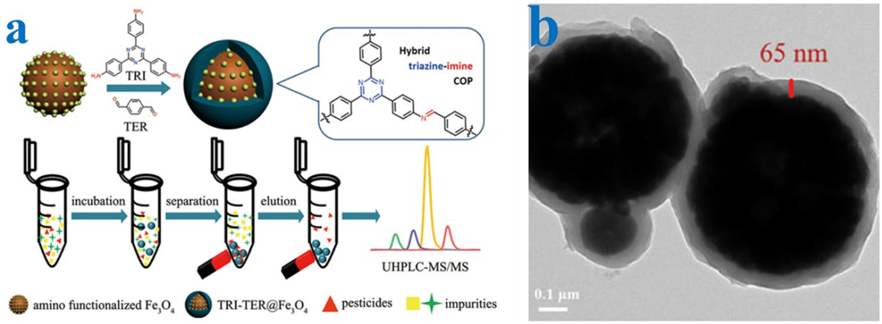


Fig. 11 **a** Schematic diagram of 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)trianiline-terephthalaldehyde@Fe_3O_4 fabrication and MSPE pretreatment procedure; **b** TEM images [72]

[74]. Liang et al. prepared a novel hybrid triazine-imine core–shell magnetic covalent organic polymer (Fig. 11a) with high adsorption capacity and excellent stability through surface-assisted in situ growth technique [75]. The core–shell structure is shown in Fig. 11b, and the polymer thickness is about 65 nm. Coupled with UHPLC-MS/MS, the analytical procedure was developed for simultaneous detection of eight pesticides in fruit. In order to simultaneously extract both acidic and alkaline pesticides, triazine-based polymeric network modified magnetic nanoparticles/GO nanocomposites were synthesized, in which the carboxyl groups of GO and the amino groups of triazinyl interacted with analytes. The imidacloprid and 2,4-dichlorophenoxyacetic acid from water and vegetable were detected by the established analytical method [76]. Wang et al. prepared magnetic porous covalent triazine-based organic polymer by *co*-precipitation to extract carbamate pesticides [77]. By investigating the main influencing factors, the analytical method was established. Because MS was used in the detection of lemonade and grape juice samples, the LODs of the method were as low as 0.02–0.20 ng mL^{-1} and 0.04–0.30 ng mL^{-1}, respectively.

3.2.3 Covalent Triazine Frameworks as Adsorbents

In order to concentrate and detect trace perfluorinated compounds in water samples, Ren et al. prepared CTF/Fe_2O_3 microspheres by 1,4-dicyanobenzene and $FeCl_3 \cdot 6H_2O$ [78]. XRD characterization indicated that the material was successfully synthesized. Furthermore, on the rough surface, a large number of pores and the high surface area (864.53 m^2 g^{-1}) were observed by SEM, TEM and BET, respectively. The CTF/Fe_2O_3-based MSPE-HPLC–MS/MS method successfully detected water quality in local ponds. Compared with the extraction methods based on other materials (ethylene glycol modified silicone, oasis HLB, C18, oasis HLB Plus and magnetic mesoporous microspheres), this method had higher sensitivity, due to the electrostatic interaction between the triazine groups and the perfluorinated compounds. After this work, another method based on this

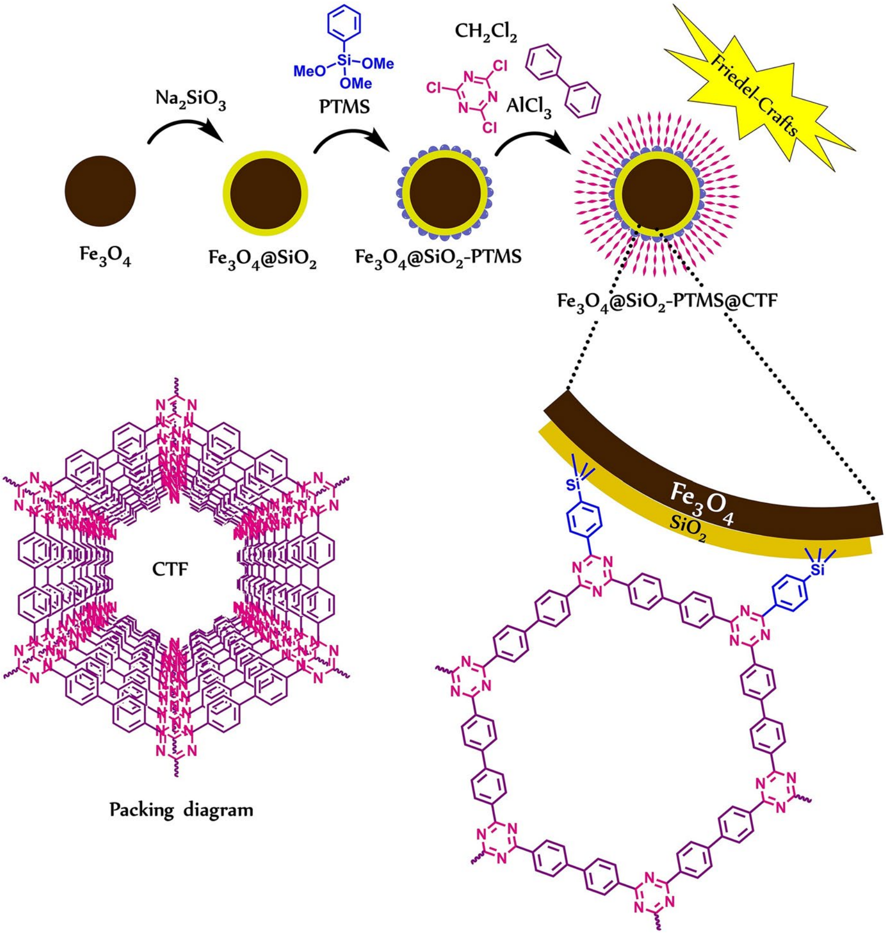


Fig. 12 Schematic representation of the synthesis of covalent triazine-based framework grafted magnetic particles and the extended CTF [80]

material was also successfully established to the quantification of phenol pollutants in water samples [79]. As shown in Fig. 12, Shahvar et al. synthesized a new CTF by Friedel–Crafts reaction between cyanuric chloride and biphenyl. In order to facilitate the material recycling, Fe_3O_4 was wrapped inside the material. This material was successfully utilized to determine parabens in breast milk, human urine, shower wastewater, sunscreen cream and herbal hair tonic by HPLC–UV [80]. Yan et al. used terephthalonitrile as the reactant to synthesize CTF by solvothermal method, and reduced it by Ni to prepare the CTF/Ni composite material. The composite material-based MSPE-gas chromatography-flame ionization detector (GC-FID) method had a short extraction time (25 min), low LODs (0.15–0.53 μg/L) and high F_E (59–88) to six phthalate esters from environmental samples [81].

3.3 Solid-Phase Microextraction

SPME combines sampling, enrichment, purification and sample injection into one single step, which can achieve high sensitivity, is a rapid test, consumes only a small amount of sample, uses non-solvent or less-solvent sample preparation, and is facile and even online coupled with chromatographic detection. On the basis of these advantages, SPME are superior to SPE and MSPE, and it has attracted increasing attention. The recent applications of triazine-based adsorbents for solid-phase microextraction are listed in Table 3.

3.3.1 Triazine-Based Polymers as Coatings

Triazine-based porous organic frameworks with different pore volumes were constructed by adjusting the proportion of cyanuric chloride and triphenylamine in the Friedel–Crafts reaction. The SPME fiber coated with the material extracted organochlorine pesticides, the results showed that the larger pore volumes, the better the extraction effect. After the main conditions were optimized, an analytical method was established by the fiber coupling with GC-ECD, and the LOD of this method was lower than 0.043 ng g^{-1}. Because the material had good stability, the fiber still had a high extraction capacity after 100 runs [82]. A triazine-based polymer was prepared on the surface of SiO_2 nanospheres by Schiff-Base reaction using melamine and *p*-terephthalaldehyde. The material was coated on stainless steel wires and packed in a polyetheretherketone (PEEK) tube for in-tube SPME of PAHs. The quantitative determination of the analytes was online achieved by connecting in-tube SPME to HPLC–DAD [83].

3.3.2 Triazine-Based Organic Aerogels as Coatings

Several triazine-based organic aerogels were developed as the coatings for SPME by Sun's group. Basalt fibers were immersed in a mixed reaction solution between melamine and formaldehyde, and the sol–gel process was carried out at 80 °C by Schiff-Base reaction of the aldehyde group with the amino group [84]. Aerogels were obtained after organic solvent displacement and drying. The fibers coated with melamine–formaldehyde aerogel were then placed into 30 cm length of PEEK tube, which was connected with HPLC for constructing online analytical system. The main factors were optimized and the in-tube SPME-HPLC–DAD method for PAHs was established. The method showed wide linear ranges (0.03–25.0 μg L^{-1}), low LODs (0.01–0.05 μg L^{-1}) and satisfactory repeatability (RSDs, 0.77–2.04%). During the synthesis process, boron nitride nanosheets were doped in the reaction solution, then boron nitride/melamine–formaldehyde composite aerogel was obtained [85]. The composite aerogel-coated wires were put into a PEEK tube to get an extraction tube. The tube was coupled to HPLC to obtain online extraction and detection of trace PAH targets. The carbon fibers with good mechanical strength were selected as the support instead of basalt fibers, and the aerogel was modified with polydopamine to effectively improve the stability and adsorption efficiency (in Fig. 13a) [86].

Table 3 The recent applications of triazine-based adsorbents for solid-phase microextraction

Adsorbents	Analytes	lods (μg l^{-1})	Linear ranges (μg L^{-1})	Samples	Detection methods	Ref
Triazine-based porous organic frameworks	Six organochlorine pesticides	0.032 ng g^{-1}	0.11–20 ng g^{-1}	Fruit samples	GC-μECD/MS	[82]
Triazine-based organic polymers@SiO_2 nanospheres	Eight PAHs	0.003	0.01–20	Water samples	HPLC–DAD	[83]
Melamine–formaldehyde aerogel	Eight PAHs	0.01	0.03–25	Water samples	HPLC–DAD	[84]
Melamine–formaldehyde aerogel doped with boron nitride nanosheets	Eight PAHs	0.005	0.03–20	Water samples	HPLC–DAD	[85]
Melamine–formaldehyde aerogel functionalized with polydopamine	Seven phthalate esters	0.02	0.07–30	Water samples	HPLC–DAD	[86]
Ionic liquid-modified melamine–formaldehyde aerogel	Five estrogens	0.05	0.15–20	Water samples	HPLC–DAD	[87]
Triazine based organic framework with micropores and mesopores	Nine phthalate esters	0.01	0.1–100	Juice samples	GC-FID	[88]

Six organochlorine pesticides: trifluralin, hexachlorobezene, aldrin, trans-heptachlor epoxide, *α*-endosulfan and dichlorodiphenyldichloroethylene; fruit samples: apple, peach and pear; eight PAHs: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene; seven phthalate esters: dimethyl phthalate, diethyl phthalate, diallyl phthalate, benzyl butyl phthalate, di-*n*-butyl phthalate, di-*n*-pentyl phthalate and dicyclo-hexyl phthalate; five estrogens: bisphenol A, 17α-ethylestradiol, estrone, diethylstillbestrol and hexestrol; Nine phthalate esters: dimethyl phthalate, diethyl phthalate, di-propyl ortho-phthalate, diallyl phthalate, dibutyl phthalate, di-2-ethylhexyl phthalate, dicyclohexyl phthalate, di-*n*-decyl phthalate, dipropyl phthalate

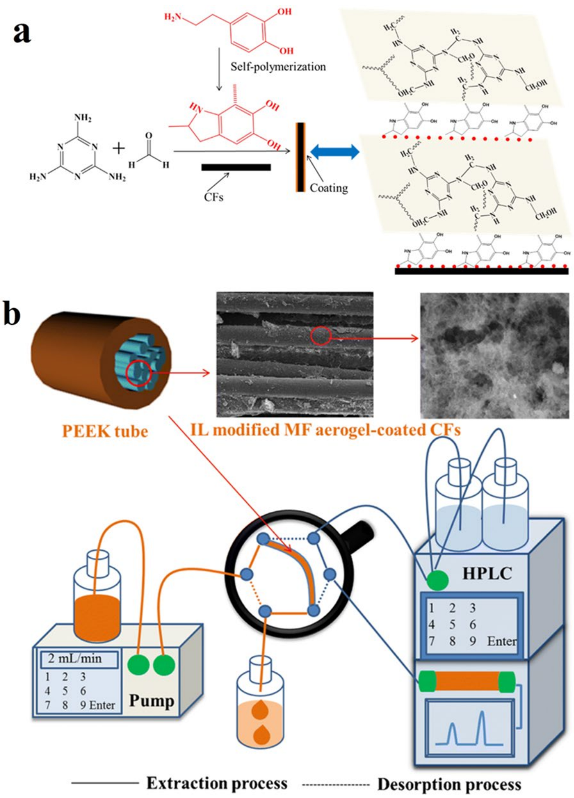


Fig. 13 **a** Synthesis of polydopamine functionalized melamine–formaldehyde aerogel [86]; **b** procedure of in-tube SPME [87]

It exhibited good extraction performance to seven phthalate esters, providing high enrichment factors in 499–3276. Such large enrichment effect could lead to high sensitivity, therefore an online sensitive in-tube SPME-HPLC–DAD method was established with low LODs in 0.02–0.05 μg L^{-1} and wide linear ranges (0.07–30 μg L^{-1}) under optimized conditions. Compared with carbon fibers and aerogel-coated carbon fibers, the functionalization of dopamine significantly improved the extraction performance. Environmentally friendly ionic liquids with excellent extractive properties were also introduced into the aerogel. 1-Dodecyl-3-(3-aminopropyl)imidazolium bromide was bonded into the melamine–formaldehyde aerogel, and the electrostatic, hydrophilic and π–π stacking mechanism of the material was demonstrated during the extraction of estrogens (shown in Fig. 13b). The established SPME-HPLC–DAD method provided low LODs (< 0.20 μg L^{-1}), wide linearity (0.15–20 μg L^{-1}), high F_E (1028–1256), satisfactory extraction repeatability (RSDs < 2.5%) and preparation reproducibility (RSDs < 10.5%) [87]. These studies not only developed organic aerogel-based adsorbents for sample preparation but also promoted triazine-based polymers for further applications.

3.3.3 Covalent Triazine Frameworks as Coatings

A dual-pore CTF that contains micropores and mesopores was prepared from 2,4,6-triphenoxy-1,3,5-triazine [88], Guo et al. applied the dual-pore CTF as the coating for headspace SPME towards phthalate esters. BET investigation indicated that the material had a high specific surface area (485 m^2 g^{-1}). The TGA analysis showed the material had no significant weightlessness below 340 °C, which was very important for the thermal desorption of the fiber in GC injector. Compared with polydimethylsiloxane (PDMS) fiber, this fiber possessed better extraction efficiencies to phthalate esters by factors between 1.08 and 40.7. The SPME-GC method was developed and used to detect phthalate esters in three kinds of fruit juices on the market. Unfortunately, the selectivity of this method for targets should be further improved.

3.4 Stir Bar Sorptive Extraction

SBSE is based on a stirring rod-shaped sorbent material in sample matrix [18], in which an extraction coating is wrapped onto a magnetic core. Because of hydrophobic, hydrogen bonding and π–π stacking forces of triazinyl groups with phenolic compounds, so CTF should have good extraction ability for phenols. Hu's group synthesized the CTF via trimerization reaction with 1,4-dicyanobenzene as reactant in melting state of $ZnCl_2$ at 400 °C for 40 h. Then a PDMS/CTF coating was prepared on the surface of capillary glass rod with iron wire by sol–gel method. It was used as a stirring rod for extracting eight phenols [89]. After optimizing the pH, ionic strength, extraction time, stirring rate, type of desorption solvent and desorption time of the samples, an efficient and sensitive SBSE method followed with HPLC detection was established, with a low LOD of 0.08 μg L^{-1}, a wide linear range of 0.25–500 μg L^{-1}, and F_E more than 65. Compared with commercial PDMS and poly(ethylene glycol), the PDMS/CTF coating showed better extraction ability. Eventually, it was used to determine phenols in Yangtze river water and east lake water.

4 Conclusions and Future Prospects

Recent years have witnessed numerous reports of triazine-based materials, the development of triazine-based materials, and the gradually maturation of their synthetic and functional methods. These achievements pave their ways to versatile applications include chemical sensing, chromatographic analysis, catalysis and drug controlled release, especially adsorption-based extraction. This paper has reviewed the recent studies on triazine-based materials in various adsorption-based extraction, containing SPE, MSPE, SPME and SBSE. As the extraction phases, triazine-based adsorbents (triazine-functionalized silica, triazine-functionalized composites, triazine-based polymers, melamine foam, triazine-based aerogels and CTFs) presented good adsorption performance towards many types of targets, such as antibiotics, heavy metal ions, PAHs, pesticide residues, plasticizers, plant hormones from water, fruit, urine, milk, juice, oils, plastic packaging and vegetable samples, owing to multiple adsorption mechanism like as π–π, chelation, hydrogen bonding, electrostatic, hydrophobic and hydrophilic interactions.

Although triazine-based materials have made some achievements in analytical chemistry, but the exploration on triazine-based materials in adsorption-based extraction is still in its infancy and facing great challenging. New preparation methods and more triazine-based materials should be interested in the future research. The reports about a simple and rapid synthesis of the CTF materials are missing and their irregular shape of a particle greatly suppress their performance as extraction phase. CTFs and triazine-based MOFs are very promising star materials, should be further explored in adsorption-based extraction field. Based on the understanding of structure-performance relationships, more studies on the CTFs should be performed. In addition, the CTFs functionalized by other components are rare, so the combination of CTFs with other functional materials (ionic liquids, graphene, metal–organic frameworks, etc.) is still a potential way to expand CTF applications in the field of adsorption-based extraction. The functionalization of CTFs with other materials or the modification of other materials with CTFs will open a broad space for developing advanced materials for specific purposes. In separation science such as chromatographic separation, pollutant removal, water purification and gas separation, there is still very widespread application space for CTFs and other triazine-based materials. Above all, triazine-based materials are promising materials in adsorption-based extraction and other fields.

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Declarations

Conflict of interest The authors have declared no conflict of interest.

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