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ADVANCED MATERIALS AS ADSORBENTS IN MICROEXTRACTIONS FOR THE DETERMINATION OF CONTAMINANTS: A MINI REVIEW

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5

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7

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ABSTRACT

The widespread presence of contaminants in water demands reliable and practical analytical methods to monitor them. However, before their determination, a sample pretreatment step is necessary. This has conventionally been performed using liquid-liquid extraction (LLE) or solid-phase extraction (SPE). Advances in material sciences have since been capitalized on, with new adsorbents used in conjunction with new sample pretreatment techniques based on microextractions. In this mini-review, we showcase some of our previously reported work that demonstrates how advanced materials such as graphene, molecularly imprinted polymers (MIPs), and polymeric cyclodextrins can be used as adsorbents for the determination of contaminants such as bisphenol A, steroids, sulfonamide antibiotics, and antimicrobial agents. These adsorbents formed an important component in the micro-solid phase extraction that was used for the pretreatment of the sample. A brief introduction to the adsorbents studied and evolution of extractions is provided. The distinctive features of the analytical methods used in the real sample analysis of the stated contaminants are highlighted.

Keywords: Advanced materials; Analytical determination; Contaminants; Sample pretreatment

1. INTRODUCTION

The presence of environmental pollutants such as herbicides, pharmaceutical waste, heavy metals (Kusumaningsih et al., 2012), and dyes (Mamat et al., 2018; Anuar et al., 2019) at trace levels has been the cause of much concern among the public and authorities. This has provided motivation for researchers to explore new materials that can be used for their removal. In analytical determination protocols, the use of these materials as adsorbents in sample preparation techniques has been keenly studied. Sample preparation is an important step in selectively isolating the analyte of interest from the sample before the analytical determination (normally using chromatographic methods). It also helps to preconcentrate the analytes, which is important in trace determinations. To achieve these objectives, extraction of the targeted analyte can be conducted using extractions (see section 3), and extractions using solid adsorbents have been viewed as the way forward. The prime objective is to introduce new

7

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materials that are more selective and easily prepared, which can improve on the conventional methods. Advanced materials have been used in numerous applications such as the determination of parabens (Fumes & Lanças, 2016), sulfonamides (Rozaini et al., 2019), bisphenol A (Rozaini et al., 2017), triclosan (Alshishani et al., 2019), and endogenous steroids (Manaf et al., 2018) in both environmental waters and human urine. Another important objective is to reduce the consumption of organic solvents, which are used in large amounts in conventional liquid-liquid extraction (LLE). In this report, the use of graphene, molecularly imprinted polymers (MIPs), and polymers containing immobilized cyclodextrin (CD) are provided as examples of how these advanced materials can be used as adsorbents in sample microextractions before their analytical determination.

2. ADSORBENTS IN MICROEXTRACTIONS

A brief introduction to the adsorbents used in this review is next presented.

2.1. Graphene

Graphene Figure 1a is a form of carbonaceous material that possesses either a single or several layers' thickness of sp^2 -hybridized carbon atoms arranged in a honeycomb pattern with large surface area. It is typically prepared according to Hummer's method through the oxidation of graphite to graphene oxide and then the further reduction of graphene oxide to graphene using a suitable reducing agent such as hydrazine (Hummers & Offeman, 1958). Furthermore, graphene has a rich in delocalized π electrons system, which contributes to its strong affinity toward pollutants that contain aromatic rings, as commonly found in pharmaceutical and veterinary drugs, pesticides, and herbicides (de Toffoli et al., 2018). Apart from that, graphene also has appealing physical and chemical properties that make it suitable for use as an adsorbent for microextractions. Graphene has been widely applied in various microextraction modes such as micro-solid phase extraction (μ -SPE) (Alshishani et al., 2019), microextraction by packed sorbents (MEPS) (Fumes & Lanças, 2016) and others.

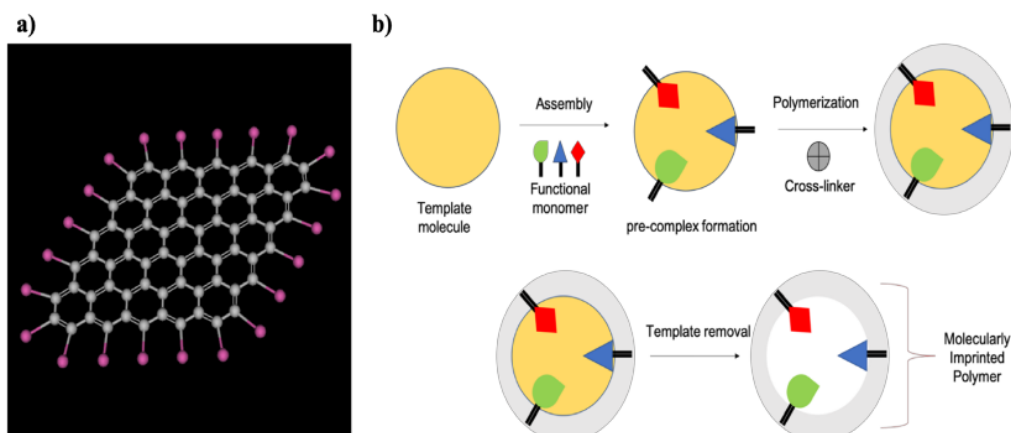


Figure 1 (a) Three-dimensional structure of graphene; (b) Typical synthesis pathway of MIPs

2.2. Molecularly Imprinted Polymers (MIPs)

The next material to have shown great potential in microextractions is MIP. This is a unique polymer that has gone through an imprinting process in which the specific target analyte (template) is imprinted to create a specific recognition site within the polymer, thus making it selective toward the target analytes. The molecular recognition is similar to the 'lock and key mechanism' typical of enzyme-substrate recognition (Figure 1b). Various imprinting

techniques have been developed for synthesizing MIPs, such as bulk precipitation, emulsion, solid-phase-based, and surface-imprinting polymerization. Among these, bulk polymerization is the simplest, wherein large particle monoliths are ground into smaller microspheres (Ashley et al., 2017). Nevertheless, as a method it produces a lower yield and requires a large amount of template for use in the imprinting process, thereby rendering it uneconomical for practical applications. Recently, several reported methods have favored the use of solid-phase-based and surface-imprinting polymer (Junjie et al., 2013). Both techniques involved the imprinting of template on a solid medium such as silica, magnetic nanoparticles, or fiber as the imprinted surface. This method shows promising results with higher yields, a reduction in the amount of template used and the involvement of simple synthesis steps. MIP has been applied as an adsorbent in the determination of trace-level pollutants in the environment such as water (Rozaini et al., 2019) and sediments (Duan et al., 2013)

2.3. Cyclodextrins (CDs)

CDs are cyclic, non-reducing oligosaccharides, consisting of d-glucopyranose units, which are bonded through α -1, 4 linkages (Cserhádi & Forgacs, 2003). CDs are obtained from enzymatic degradation of starch (Crini, 2014). CDs can be categorized according to the number of glucose units, i.e., α -CD (consist of six), β -CD (seven), and γ -CD with eight glucose units. CDs orient themselves and form a toroidal truncated cone structure (Figure 2) where the cavity is lined by hydrogen atoms and glycosidic oxygen bridges. The non-bonding electron pairs are directed inside the cavity, resulting in high electron density (Cserhádi & Forgacs, 2003). β -CD has the lowest solubility in water compared to the others due to the presence of a complete secondary belt that is formed due to the ability of the hydroxyl group from C-2 to form a hydrogen bond with the hydroxyl group in C₃, while the hydrogen belt in α -CD is incomplete due to the distorted position of one glucopyranose unit (Cserhádi & Forgacs, 2003). The most distinctive characteristic of CD is its ability to form host-guest inclusion complexes by capturing various types of guest compounds with suitable properties inside its cavity (Tian et al., 2012). The formation of inclusion complexes depends on the interaction between CD and guest molecules, the type of CD used (e.g., α , β , or γ), the method by which the inclusion complex is prepared, and the type of guest molecules (Crini, 2014). CDs are also environmentally friendly and soluble in water, which improves the solubility and dispersibility of the material (Mahpishanian & Sereshti, 2017). In separation chemistry, β -CD is usually chosen as an adsorbent in comparison to others due to its lower solubility. In addition, β -CD is easily available and cost-effective (Del Valle, 2004). β -CD has been used for the determination and removal of different types of analytes such as organochlorine pesticides (Tian et al., 2012; Mahpishanian & Sereshti, 2017), endogenous steroids (Manaf et al., 2018) and others.

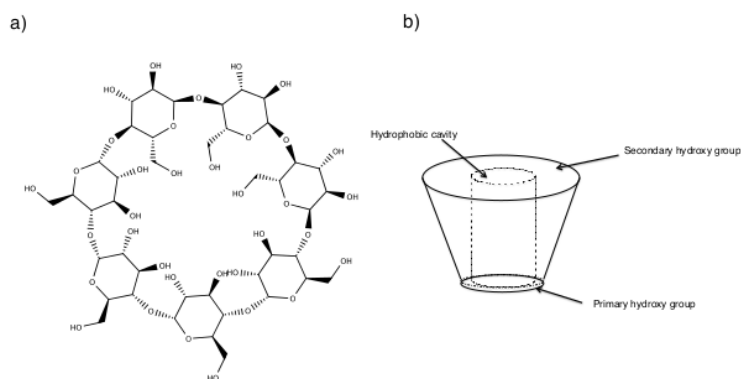


Figure 2 (a) Chemical structure of β -cyclodextrin; (b) Toroidal truncated cone structure of cyclodextrin

3. EVOLUTION OF EXTRACTION METHODS

Analytical methods of analysis involve several steps such as sampling, sample preparation, extraction and isolation of target analytes, and the separation, detection and quantification of analytes. Of all these steps, sample preparation plays a significant role in determining the quality of the result and the time required for that particular analysis. LLE was one of the earliest extraction methods used. The LLE technique involves the distribution of analyte between two water-immiscible solvents. This technique is largely dependent on the mass transfer of the target analyte from the first liquid phase (normally an aqueous phase containing the analyte) into a second liquid phase (normally an organic solvent) (Müller et al., 2008). In order to facilitate the mass transfer, the organic phase will be dispersed into the aqueous solution phase to form tiny droplets, thereby increasing the contact surface area. It is common to provide external energy (e.g., vortex, mixing) to accelerate the mass transfer (Müller et al., 2008).

SPE is another conventional extraction method based on the affinity of the target analyte toward an adsorbent. The sample solution containing the analyte (mobile phase) will be allowed to pass through a solid adsorbent (stationary phase). The target analyte is retained in the stationary phase due to the affinity of the analyte for the adsorbent. An eluting solvent is next passed through the column to elute the analyte from the adsorbent surface. The eluted analyte can then be analyzed using a suitable analytical method such as gas chromatography or high performance liquid chromatography (HPLC). The main advantages of SPE compared to LLE are the ability of SPE to extract a wide range of organic pollutants from various kinds of samples (e.g., biological, environmental water). Apart from that, the use of SPE cartridges help to prevent the analyte from decomposing, hence enabling it to be stored for a longer duration without compromising the integrity of the sample (Andrade-Eiroa et al., 2016). However, SPE suffers from a lack of selectivity in determining organic pollutants. Thus, in the past decades, various modifications have been made to the SPE method, aimed at simplicity, miniaturization, and automation. One of the proposed alternatives was the introduction of (μ -SPE) and mixed matrix membrane (MMM) microextraction methods.

The μ -SPE technique was introduced in 2006 by Basheer et al. (2006) for the determination of organophosphorus pesticides. In this technique, a porous membrane is used as a packed membrane (μ -SPE device) with a small quantity of adsorbent (about 10 mg) introduced into it. The membrane acts as a physical barrier between the analyte solution and the adsorbent. The main advantage of using a porous membrane is that it will act as a filter and protect the adsorbent from matrix components that can interfere in the analytical determination. Aside from that, it enables clean-up and preconcentration of the extraction to be performed in one step (Sajid, 2017), thus reducing the analysis time.

MMM comprises homogeneous particles that have been dispersed in a polymer matrix (Kamaruzaman et al., 2013). One way of preparing MMM is to use the phase inversion method where the casting mixture is dissolved simultaneously with the polymer matrix (Kamaruzaman et al., 2013). The adsorbents are usually introduced to the polymer matrix prior to drying in order to incorporate the adsorbent with the polymer matrix. The presence of adsorbent particles in the membrane gives the membrane additional mechanical strength (Kamaruzaman et al., 2013). The application of MMM in extraction methods is capable of reducing analysis time by simplifying the adsorbent retrieval steps and removing the filtration steps. Besides, since the thickness of MMM is around 1 mm (Rozaini et al., 2019), only a minute amount of solvent (μ L) is required for the desorption process (retrieving the analyte from adsorbent to solvent prior to the instrumental analysis). In the next section, we will summarize some of our

reported work involving the use of advanced materials as adsorbent when applied in the μ -SPE and MMM techniques.

4. ANALYTICAL APPLICATIONS

4.1. HPLC Determination of Triclosan, Triclocarban and Methyl-triclosan in Wastewater using Mini-bar Micro-solid Phase Extraction with Graphene as Adsorbent

Alshishani et al. (2019) developed an interesting microextraction technique where graphene was used as an adsorbent for the determination of three antimicrobial agents, triclosan (TCS), triclocarban (TCC), and methyl-triclosan (MTCS), in wastewater. There is concern regarding the use of these antimicrobials in common personal care items such as hand wash, shampoos, etc. due to their similarity to the known endocrine disruptor, steroids. Thus, there is a need to monitor the levels of these compounds in environmental waters. In this technique, 20 mg of graphene was packed inside a porous polypropylene (PP) bag (1.5 cm \times 0.8 cm), which was then placed inside a bigger PP bag (2.0 cm \times 0.8 cm) that contained a metal rod (Figure 3). The metal rod was necessary to ensure the device would remain at the base of the sample vial for the duration of the extraction process. During the extraction, the compounds were able to diffuse through the membrane and be adsorbed by the graphene. After the extraction, the adsorbed antimicrobial agents were desorbed using suitable solvents and an aliquot was injected into an HPLC unit for the separation and determination. Various analytical parameters were investigated with a linear range of 0.2–1000 μgL^{-1} . The limit of detection (LOD) values obtained for TCS, TCC, and MTCS were 0.07, 0.04, and 0.06 μgL^{-1} , while the limit of quantification (LOQ) values were 0.22, 0.13, and 0.17 μgL^{-1} , respectively. The recoveries obtained for the three different concentrations (2, 50 and 500 μgL^{-1}) were from 80% to 86.5% (TCS), 86.0% to 100% (TCC), and 93.7% to 96.6% (MTCS). Good precision (inter/intra) was achieved with a % relative standard deviation (RSD %) of less than 20 (n = 5). The developed method was applied to the determination of TCS, TCC, and MTCS in wastewater samples.

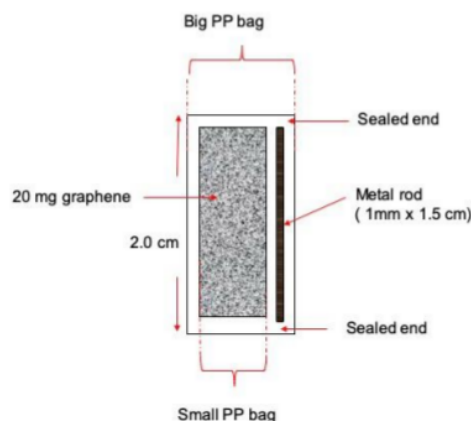


Figure 3 Mini-bar micro-SPE device containing graphene as adsorbent

4.2. HPLC Determination of Sulfonamide Antibiotics in Water Samples using Molecularly Imprinted Silica Gel Incorporated with Agarose Polymer Membrane

A microextraction technique using molecularly imprinted silica gel (MISG) has been developed and reported for the determination of several sulfonamide antibiotics (sulfamethoxazole (SMX), sulfamonomethoxine (SMM), and sulfadiazine (SDZ)) in water samples (Rozaini et al., 2019). Sulfonamide antibiotics (SAs) are widely used as veterinary

drugs in livestock farming. While trace levels of SAs have been found in animal-based products (Costi et al., 2010), there is also concern regarding the presence of SAs in environmental water. SMX was used as the template for MISG. In this method, 15 mg of MISG was incorporated with agarose polymer and used as membrane adsorbent (thickness; 1.0 mm, diameter; 1.0 cm). The membrane acts as a matrix to immobilize the MISG. This technique simplifies the adsorbent collection and desorption process to one that does not include any centrifugation or filtration steps. After selective extraction followed by desorption, the extracts are subjected to HPLC analysis. Several analytical parameters were evaluated with linearity range 1–500 $\mu\text{g L}^{-1}$. The LODs obtained for SMX, SMM, and SDZ were 0.06, 0.17, and 0.15 $\mu\text{g L}^{-1}$, while the LOQs achieved were 0.20, 0.56, and 0.50 $\mu\text{g L}^{-1}$, respectively. Furthermore, this method showed good relative recoveries (80–96%) and %RSD (< 10%). Apart from that, a selectivity study was carried out to determine the selectivity of MISG toward analytes that have almost similar chemical structures (i.e., sulfacetamide (SCM), sulfamethazine (SMZ)) with the template compound (SMX). The selectivity coefficient (K) for SMX was found to be the highest compared to the other drugs, thus suggesting that MISG has good selectivity towards the target analyte. The developed method was applied to the determination of SMX, SMM, and SDZ in tap and river waters.

4.3. HPLC Determination of Bisphenol A in Water using Micro-solid Phase Extraction with Molecularly Imprinted Polymer Adsorbent

A simple, rapid, cost-effective, and environmentally friendly sample preparation technique has been developed using MIP for the determination of bisphenol A in environmental water (Rozaini et al., 2017). Bisphenol A is a compound classified as an endocrine-disrupting compound (EDC). The ability of bisphenol A to mimic human endogenous hormone has raised concern due to the potential hazard arising from unintended contact with environmental water by humans. In this technique, a small amount of MIP (4 mg) was packed into a polypropylene membrane with an equilateral triangle-shaped membrane (1cm \times 1cm) to create a μ -SPE device. The extraction was aided by ultrasound emulsification prior to the HPLC determination. This method shows good linearity (0.5–700 $\mu\text{g L}^{-1}$), low LOD (0.07 $\mu\text{g L}^{-1}$), and good analyte recoveries (82.2–118.9%) with an RSD range of 0.7–14.2%. The good selectivity enabled this method to be applied to the determination of bisphenol A in 30 samples, including various kinds of water such as drinking, mineral, river, and lake water. Beverages and canned food samples were also tested.

4.4. LC-MS/MS Determination of Steroids in Urine using Micro-solid Phase Extraction with Polymeric Cyclodextrins as Adsorbent

Manaf et al. (2018) described the preparation of novel polymers that were prepared by cross-linking β -cyclodextrin (β -CD) with different cross-linkers (herein referred to as CD polymer). The CD polymer was used as an adsorbent for the μ -SPE of steroids in the urine of volunteers prior to the LC-MS/MS analysis. Steroids are important compounds that play a vital role in sexual maturation, physical development, and other metabolisms. The determination of steroids is also used in the diagnosis of diseases such as Alzheimer's and liver cancer (Zhang et al., 2019). The World Anti-Doping Agency, as part of the fight against drug abuse among athletes, requires testing for a "steroid profile" composed of testosterone (T), epitestosterone (E), androsterone (A), etiocholanolone (Etio), 5 α -dihydrotestosterone-3 α ,17 β -diol (5 α Adiol), and 5 β -androstane-3 α ,17 β -diol (5 β Adiol), along with the ratio of T to E (T/E) (Manaf et al., 2018). Due to the many areas that require information on steroids, reliable analytical methods are thus required. Due to the low concentrations of steroids in typical samples, sensitive methods are necessary. Due to their excellent sensitivity, gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) are the predominant methods used. However, between these two techniques, LC-MS/MS is preferred as GC-MS

normally requires a derivatization step prior to the detection. Even for a sophisticated MS/MS instrument, sample preparation is normally required, especially to overcome ionization interferences. And typical of any solid phase extraction, the selection of adsorbent is also vital in the μ -SPE method. Of the adsorbents tested, CD polymer showed the best adsorption properties toward the steroids tested, even outperforming the commercial C18 and Plexa adsorbents. The method was optimized for important parameters, and the adopted parameters are summarized in Table 1. All the steroids of interest were found in all the urine samples analyzed. As expected, with the exception of E, elevated levels of the steroids were found in sample C (steroid elimination urine). No interference peak was detected at the expected retention time of the steroids in the artificial urine sample, indicating that the method was specific for the analytes of interest. The method used remarkably few organic solvents compared to the LLE method. The method is also faster (1.5 h) in comparison to the standard SPE method (6 h), including hydrolysis and analysis. Another major advantage of this technique over the standard method is that chemical derivatization is not required.

Table 1 (a) Adopted parameters for the μ -SPE-LC-MS/MS determination of steroids; (b) level of steroid found in urine samples using μ -SPE-LC-MS/MS method (Manaf et al., 2018)

Parameter	Adopted conditions	Steroid	Urine Samples			Maximum Allowed by WADA
			A (Quality Control)	B (Healthy Volunteer)	C (Steroid Elimination Urine)	
Type of adsorbent	CD polymer	T	29	38	247	200
Desorption solvent	Acetonitrile	E	6.6	41	37	200
Ultrasonication time	30 min	Etio	4312	1873	17,369	10,000
Desorption solvent	300 μ L	A	5110	2966	28,493	10,000
Sonication time for desorption	20 min	5 α Adiol	205	133	594	250
Mass of CD polymer adsorbent	5 mg	5 β Adiol	107	191	568	-
Sample volume	3 mL	T/E ratio	4.4	0.9	6.8	4.0

5. CONCLUSION

Advanced materials, due to their unique properties, have proven to be useful in numerous applications. We demonstrated how MIP, graphene, and CD were used as adsorbents for the microextraction of model antimicrobials, steroids, and veterinary drugs. The analytical techniques that resulted from these innovations were simple, effective, conserve solvents and materials, which support the green analytical chemistry initiatives.

6. ACKNOWLEDGEMENT

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