Brazilian Journal of Analytical Chemistry
doi: 10.30744/brjac.2179-3425.letter.prichter1

LETTER

Developing Green Sorbents Derived from Natural Materials for Microextraction and Determination of Emerging Contaminants

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Microextraction technologies emerged as an attractive and eco-efficient alternative in sample preparation with the advent of solid-phase microextraction (SPME).[1] The sensitivity and precision of methodologies based on microextraction are improving due to the ease of preconcentration and automation capacity that they provide, respectively. Furthermore, the miniaturization and eco-efficiency have improved considerably by using less space and avoiding the use of toxic reagents and high volumes of organic solvents.

From the 1990s until the present, SPME has continued to evolve, becoming commercially available for many chromatographic applications. Also in this period, stir bar sorptive extraction (SBSE) has become another commercially available alternative,[2] with the extraction device offering a greater volume of sorbent phase compared to SPME. Simultaneously, other novel microextraction techniques have emerged that complement some of the drawbacks of SBSE.[3] Among these microextraction techniques, rotating-disk sorptive extraction (RDSE) was proposed by our research group in 2009 and has been recently reviewed, considering all its advances and applications.[4,5]

The heart of all microextraction technologies is the nature of the sorbent phase. In the context of solid sorbents, they can be classified as synthetic or natural materials according to their origin (Figure 1). Typical examples of synthetic sorbents range from the most hydrophobic octadecyl (C18) to the ion exchange phases, most of them being commercially available. Sorbents of intermediate polarity (hydrophilic–lipophilic balance) and hydrophilic-like silica-based sorbents are also commercially available. In the specific case of emerging contaminants, the copolymer of divinylbenzene and *N*-vinylpyrrolidone (Oasis™ HLB) has largely been used, considering that its hydrophilic–lipophilic balance allows various sorption interactions with emerging contaminants. Among them, hydrophobic interactions occur through π-stacking and polar interactions occur via hydrogen bonding. The hydrophilic–lipophilic balance typical of Oasis™ HLB has encouraged its use in RDSE as a sorbent in multiresidue analysis.[6,7]

Although sorbents based on these commercial polymers are being used in different microextraction techniques, some trends are currently being claimed in the design of solid sorbents by considering new synthetic materials. In this context, micro- and nanomaterials have been tested, such as carbon nanotubes, graphene and fullerenes.[8] Interactions via delocalized π-electrons are especially important for molecules containing aromatic rings, as in the case of emerging contaminants. Other nonconventional materials[9] that are being actively studied as synthetic sorbents are porous solids such as metal organic frameworks, covalent organic frameworks and layered double hydroxides.

Together with these sorbent developments, the innovation in materials of natural origin, which can be recycled, is another parallel trend in analytical chemistry and is the central idea to be addressed in the

Cite: Richter, P. Developing Green Sorbents Derived from Natural Materials for Microextraction and Determination of Emerging Contaminants. *Braz. J. Anal. Chem.* (Forthcoming). https://doi.org/10.30744/brjac.2179-3425.letter.prichter1

This letter was submitted to the BrJAC special issue celebrating the achievement of an Impact Factor$_{2022}$ of 0.7.

current research of our team. As mentioned previously, a current challenge in analytical chemistry is to emphasize the use of eco-efficient or green analytical processes, positioning this characteristic at the same level as the sensitivity and selectivity of the measurement. Microextraction technology is green per se, given the minimization of the consumption of organic solvents in the sample preparation stage. However, an even higher level of analytical eco-efficiency (or greenness) is achieved when the sorbent phase used is of natural origin; in this way, the use of natural materials is in line with the change of the paradigm of typical production models (take–make–dispose) towards a circular model of waste reuse.[10]

Sorbents of natural origin can be classified according to their chemical composition as inorganic and organic sorbents. Clay is an example of an inorganic sorbent that plays an important role in the retention/mobility behavior of chemicals in the soil. Consequently, materials based on clay have been proposed as sorbents in different microextraction devices.[11] Clays can also be modified to decrease their polarity for use in the sorption of hydrophobic analytes.[11,12]

Natural organic sorbents, also called biopolymeric sorbents, can be classified by their origin as natural polymers of plant origin (polysaccharides, proteins, polyesters), animal origin (polysaccharides, proteins, resins) and microbial origin (polysaccharides, polyesters, polyamides, polyanhydrides).[13] All these materials prepared from natural biopolymers have been studied and proposed primarily in water treatment technologies; however, they could also be considered in the field of analytical chemistry as microextraction/extraction sorbents. The main novelty of this idea is that it is only recently, and in only a few cases, that these sorbents been used in microextraction technology, with wide future perspectives being expected.[10,13]

These natural materials can also be modified through known reactions of functionalization (selective oxidation, esterification, crosslinking, copolymerization, etc.). Such modifications reinforce the potential of the functional group and the number of active sites of the sorption material.[14] In addition, modification of the natural materials can be achieved by pyrolysis to produce biochar. During the pyrolysis process, the components are thermally decomposed at different temperatures and times, expanding their porosity. Besides to increase the degree of aromatic condensation and aromaticity, typical functionalities present on the biochar surface include hydroxyl, carboxylic, lactone, amine and amide moieties, which are the key to its sorptive properties[15] and the retention of pollutants of different natures. Similarly, from these natural materials, activated carbon can be generated at a significantly lower cost than from the same commercial substrate. To prepare activated carbon from these natural materials, two basic steps are required: pyrolysis of the raw material; and activation. Pyrolysis in the temperature range of 300–900 °C produces biochar with the required porosity associated with high carbon content. The activation step then provides a material with a higher surface area, generating additional porosity, and allows adjustment of the chemical surface to produce unique characteristics.[16]

During recent years, our research group has been contributing to this research field by designing new natural sorbent phases to be applied in the microextraction of emerging contaminants from wastewater and river water. Some examples of natural sorbent phases implemented in our laboratory are peanut shells,[17] cork,[18] avocado seed[19] and chitosan.[20] In various instances, these materials or their derivatives have shown comparative sorption behavior with commercial sorbents such as Oasis™ HLB. By using these natural sorbents, emerging contaminants have been quantified in wastewater and river water samples from the metropolitan region of Chile.

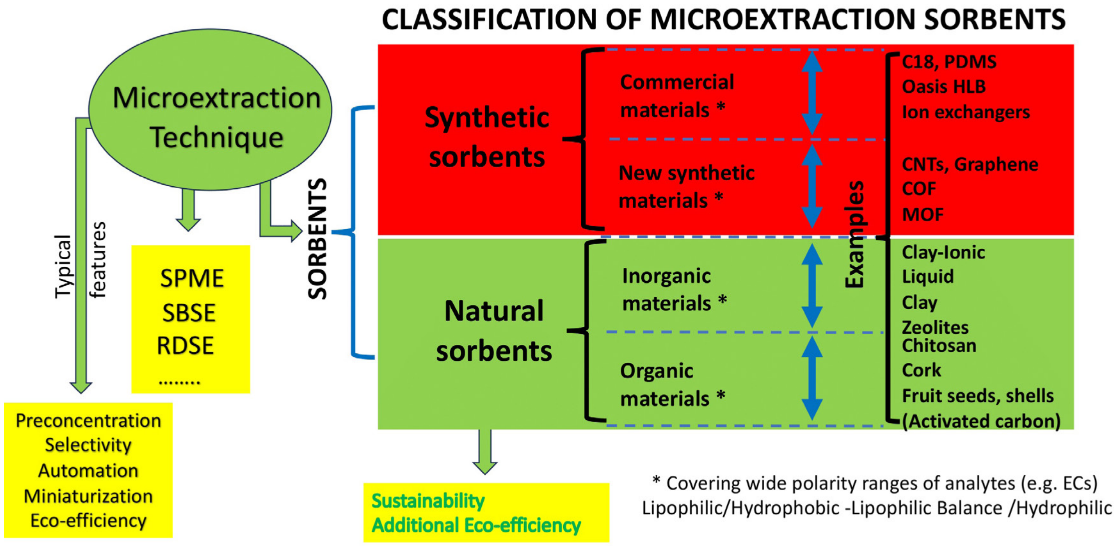

Figure 1. Classification of solid sorbents used in microextraction techniques, along with some typical features and examples.

Acknowledgements

The author thanks FONDECYT, Chile (Regular Project 1220225) and FONDEQUIP, Chile (Project EQM170141) for financial support.

REFERENCES

(1) Belardi, R. P.; Pawliszyn, J. B. The application of chemically modified fused silica fibers in the extraction of organics from water matrix samples and their rapid transfer to capillary columns. *Water Qual. Res. J.* **1989**, *24* (1), 179-191. https://doi.org/10.2166/wqrj.1989.010

(2) Baltussen, E.; Sandra, P.; David, F.; Cramers, C. Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: theory and principles. *J. Microcolumn Sep.* **1999**, *11* (10), 737–747. https://doi.org/10.1002/(SICI)1520-667X(1999)11:10<737::AID-MCS7>3.0.CO;2-4

(3) Lucena, R. Extraction and stirring integrated techniques: examples and recent advances. *Anal. Bioanal. Chem.* **2012**, *403*, 2213-2223. https://doi.org/10.1007/s00216-012-5826-9

(4) Richter, P.; Leiva, C.; Choque, C.; Giordano, A.; Sepúlveda, B. Rotating-disk sorptive extraction of nonylphenol from water samples. *J. Chromatogr. A* **2009**, *1216* (49), 8598-8602. https://doi.org/10.1016/j.chroma.2009.10.044

(5) Richter, P.; Arismendi, D.; Becerra-Herrera, M. The fundamentals, chemistries and applications of rotating-disk sorptive extraction. *TrAC, Trends Anal. Chem.* **2021**, *137*, 116209. https://doi.org/10.1016/j.trac.2021.116209

(6) Arismendi, D.; Becerra-Herrera, M.; Cerrato, I.; Richter, P. Simultaneous determination of multiresidue and multiclass emerging contaminants in waters by rotating-disk sorptive extraction–derivatization-gas chromatography/mass spectrometry. *Talanta* **2019**, *201*, 480–489. https://doi.org/10.1016/j.talanta.2019.03.120

(7) Donato, F. F.; Bandeira, N. M. G.; dos Santos, G. C.; Prestes, O. D.; Adaime, M. B.; Zanella, R. Evaluation of the rotating disk sorptive extraction technique with polymeric sorbent for multiresidue determination of pesticides in water by ultra-high-performance liquid chromatography–tandem mass spectrometry. *J. Chromatogr. A* **2017**, *1516*, 54-63. https://doi.org/10.1016/j.chroma.2017.08.025

(8) Vasconcelos, E.; Maciel, S.; Mejía-Carmona, K.; Jordan-Sinisterra, M.; da Silva, L. F.; Vargas-Medina, D. A.; Lanças, F. M. The Current Role of Graphene-Based Nanomaterials in the Sample Preparation Arena. *Front. Chem.* **2020**, *8*, 664. https://doi.org/10.3389/fchem.2020.00664

(9) Maya, F.; Palomino-Cabello, C.; Ghani, M.; Turnes-Palomino, G.; Cerdà, V. Emerging materials for sample preparation. *J. Sep. Sci.* **2018**, *41* (1), 262–287. https://doi.org/10.1002/jssc.201700836

(10) Mafra, G.; García-Valverde, M. T.; Millán-Santiago, J.; Carasek, E.; Lucena, R.; Cárdenas, S. Returning to Nature for the Design of Sorptive Phases in Solid-Phase Microextraction. *Separations* **2020**, *7* (1), 2. https://doi.org/10.3390/separations7010002

(11) Fiscal-Ladino, J. A.; Obando-Ceballos, M.; Rosero-Moreano, M.; Montaño, D. F.; Cardona, W.; Giraldo, L. F.; Richter, P. Ionic liquids intercalated in montmorillonite as the sorptive phase for the extraction of low-polarity organic compounds from water by rotating-disk sorptive extraction. *Anal. Chim. Acta* **2017**, *953*, 23-31. https://doi.org/10.1016/j.aca.2016.11.067

(12) Vieira, C. M. S.; Mazurkievicz, M.; Calvo, A. M.; Debatin, V. L.; Micke, G. A.; Richter, P.; Rosero-Moreano, M.; Rocha, E. C. D. Exploiting green sorbents in rotating-disk sorptive extraction for the determination of parabens by high-performance liquid chromatography with tandem electrospray ionization triple quadrupole mass spectrometry. *J. Separ. Sci.* **2018**, *41* (21), 4047-4054. https://doi.org/10.1002/jssc.201800426

(13) Godage, N. H.; Gionfriddo, E. Use of natural sorbents as alternative and green extractive materials: A critical review. *Anal. Chim. Acta* **2020**, *1125*, 187-200. https://doi.org/10.1016/j.aca.2020.05.045

(14) De Gisi, S.; Lofrano, G.; Grassi, M.; Notarnicola, M. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. *Sustainable Mater. Technol.* **2016**, *9*, 10–40. https://doi.org/10.1016/j.susmat.2016.06.002

(15) Yaashikaa, P. R.; Kumara, P. S.; Varjanic, S.; Saravanan, A. A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy. *Biotechnol. Rep.* **2020**, *28*, e00570. https://doi.org/10.1016/j.btre.2020.e00570

(16) Gao, Y.; Yue, Q.; Gao, B.; Li, A. Insight into activated carbon from different kinds of chemical activating agents: A review. *Sci. Total Environ.* **2020**, *746*, 141094. https://doi.org/10.1016/j.scitotenv.2020.141094

(17) Torres-Lara, N.; Molina-Balmaceda, A.; Arismendi, D.; Richter, P. Peanut shell-derived activated biochar as a convenient, low-cost, ecofriendly and efficient sorbent in rotating disk sorptive extraction of emerging contaminants from environmental water samples. *Green Analytical Chemistry* **2023**, *6*, 100073. https://doi.org/10.1016/j.greeac.2023.100073

(18) Manzo, V.; Goya-Pacheco, J.; Arismendi, D.; Becerra-Herrera, M.; Castillo-Aguirre, A.; Castillo-Felices, R.; Rosero-Moreano, M.; Carasek, E.; Richter, P. Cork sheet as a sorptive phase to extract hormones from water by rotating-disk sorptive extraction (RDSE). *Anal. Chim. Acta* **2019**, *1087*, 1-10. https://doi.org/10.1016/j.aca.2019.08.069

(19) Molina-Balmaceda, A.; Rojas-Candia, V.; Arismendi, D.; Richter, P. Activated carbon from avocado seed as sorbent phase for microextraction technologies: activation, characterization, and analytical performance. *Anal. Bioanal. Chem.* **2024**. https://doi.org/10.1007/s00216-024-05203-1

(20) Arismendi, D.; Vera, I.; Ahumada, I.; Richter, P. A thin biofilm of chitosan as a sorptive phase in the rotating disk sorptive extraction of triclosan and methyl triclosan from water samples. *Anal. Chim. Acta* **2023**, *1252*, 341053. https://doi.org/10.1016/j.aca.2023.341053

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