ZEOLITES AND ZEOLITE-BASED MATERIALS IN EXTRACTION AND MICROEXTRACTION TECHNIQUES

Paola Baile, Elena Fernández, Lorena Vidal* and Antonio Canals

Departamento de Química Analítica, Nutrición y Bromatología e Instituto Universitario de Materiales, Universidad de Alicante, P.O. Box 99, E-03080 Alicante, Spain.

*Corresponding author: Tel.: +34965903400; fax: +34965903697.

E-mail address: lorena.vidal@ua.es (L. Vidal)

Abstract

Zeolites are ordered crystalline materials with a promising performance for a wide range of applications such as catalysis, petrochemistry, environmental remediation and medicine, but scarcely evaluated in Analytical Chemistry. Their unique and fascinating properties such as high surface area, high adsorption capacity and molecular selectivity, chemical and thermal stability, ion-exchange capacity, low cost extraction and synthesis, and their easy modification, which provides a wide range of zeolite-based materials, convert zeolites in potential sorbents for extraction procedures. Therefore, in this review we provide an overview at the current status of zeolites and zeolite-based materials used in extraction and microextraction techniques with reference to recent applications and highlighting some of the novel advances.

Keywords: zeolite; zeolite-based materials; extraction; microextraction;; metals; organic compounds.

LIST OF ABBREVIATIONS

2,6-DAP	2,6-diacetyl pyridine
5-Br-PADAP	2-(5-bromo-2-pyridylazo)-5-diethylaminophenol
AChE	Acetylcholinesterase
APDC	Ammonium pyrrolidine dithiocarbamate
ASDPV	Anodic stripping differential pulse voltammetry
BDTA	Benzyldimethyltetradecylammonium
BDTA-Cl	Benzyldimethyltetradecylammonium chloride
BTEX	Benzene, toluene, ethylbenzene and xylenes
BTX	Benzene, toluene and xylenes
CC[4]A	Carboxylatocalix[4]arenes
CEC	Cation-exchange capacity
CMC	Critical micelle concentration
CTA	Cetyltrimethylammonium
CTA-Br	Cetyltrimethylammonium bromide
D-µ-SPE	Dispersive micro-solid-phase extraction
DDTC	Sodium diethyldithiocarbamate trihydrate
DHPDT	2-(3,4-dihydroxyphenyl)-1,3-dithiane
DI	Direct immersion
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DR-UV	Diffuse reflectance ultraviolet
DSPE	Dispersive solid-phase extraction
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy dispersive X-ray
ETAAS	Electrothermal atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
FDS	First-order derivative spectrophotometry
FDS-HPSAM	First-order derivative spectrophotometry-H-point standard addition method
FE-SEM	Field emission scanning electron microscopy
FI-FAAS	Flow injection flame atomic absorption spectrometry
FT-IR	Fourier Transform Infrared

G-CL	Graphene-clinoptilolite
GC-FID	Gas chromatography-flame ionization detection
GC-MS	Gas chromatography-mass spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
HDTMA	Hexadecyltrimethylammonium
HDTMA-Br	Hexadecyltrimethylammonium bromide
HPLC-PDA	High-performance liquid chromatography-photodiode array detection
HPSAM	H-point standard addition method
HS	Headspace
ICP AES	Inductively coupled plasma atomic emission spectrometry
ICP OES	Inductively coupled plasma optical emission spectrometry
IZA	International Zeolite Association
LC-FD	Liquid chromatography-fluorescence detection
LC-MWD	Liquid chromatography-multiple wavelength detection
LC-PDA	Liquid chromatography-photodiode array detection
LC-UV	Liquid chromatography-ultraviolet detection
LC-UV/FD	Liquid chromatography-ultraviolet/fluorescence detection
LETRSS	Laser-excited time-resolved Shpol´skii spectroscopy
LODs	Limits of detection
LTA	Linde Type A
LTL	Linde Type L
MIBK	Methyl isobutyl ketone
MS	Mass spectrometry
MSPE	Magnetic solid-phase extraction
Neothorin	3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalene disulfonic acid
Nitroso-S	2-nitroso-1-naphthol-4-sulfonic acid
ODTMA	Octadecyltrimethylammonium
ODTMA-Br	Octadecyltrimethylammonium bromide
PA	3-aminopropyl trimethoxy silane
PAHs	Polycyclic aromatic hydrocarbons
PAN	1-(2-pyridylazo)-2-naphtol
PANI	Polyaniline
PAR	4-(2-pyridylazo)resorcinol

PBS	Phosphate buffered saline
PMME	Polymer monolith microextraction
PTFE	Polytetrafluoroethylene
RSD	Relative standard deviation
RT	Room-temperature
Schiff base	5-((4-nitrophenylazo)-N-(2′,4′-dimethoxyphenyl))salicylaldimine
SDS-PAGE	Sodium dodecyl sulfate-polyacrylamide gel electrophoresis
SEM/EDS	Scanning electron microscopy with energy dispersive spectroscopy
SPE	Solid-phase extraction
SPME	Solid-phase microextraction
TDMBA	Tetradecyldimethylbenzylammonium
TDMBA-Cl	Tetradecyldimethylbenzylammonium chloride
TDS	Third-order derivative spectrophotometry
TFME	Thin-film microextraction
TMA	Tetramethylammonium
TMA-Br	Tetramethylammonium bromide
TMA-Cl	Tetramethylammonium chloride
TPPZ	2,3,5,6-tetra(2-pyridyl)pyrazine
UPLC-Q-TOF-MS	Ultra-high performance liquid chromatography-quadrupole time-of-flight mass spectrometry
UV-vis	Ultraviolet-visible
VOCs	Volatile organic compounds
XRD	X-ray diffraction
Zincon	2-[1-(2-hydroxy-5-sulforphenyl)-3-phenyl-5-formazano]-benzoic acid monosodium salt
ZSM-5	Zeolite Socony Mobil–5
µ-SPE	Micro-solid-phase extraction

Contents

1. Introduction

Mineralogist Cronstedt used the term zeolite for the first time in the middle of the 18th century (1756) to describe an aluminosilicate mineral (some authors identified this mineral as stilbite).[1,2] Etymologically, this term is derived from two Greek words, the word "zeo" means boiling and the word "lithos" means stone, since this mineral releases and adsorbs water once is heated and cooled, respectively.[1,3] Zeolites are naturally originated at mines and more than 60 natural zeolites are known nowadays in the world, although new zeolite minerals are constantly identified.[1] Among these natural zeolites, clinoptilolite, mordenite, phillipsite, chabazite, stilbite, analcime, laumontite and erionite are the most commonly evaluated.[4] Furthermore, zeolites can also be synthetically prepared in the laboratory and in fact the number of synthetic zeolites is constantly increasing every year. Though the existence of natural zeolites was noted about 250 years ago, this mineral was not studied in depth until 1940 with the pioneering studies of Professor Barrer and coworkers in zeolite synthesis and adsorption.[1] Today, more than 200 different structural types of zeolites are known, the majority being synthetic. All these structures have been formally recognized by the Structure Commission of the International Zeolite Association (IZA)[5] and assigned a three-letter code, the so-called Framework Type Code.[1]

Zeolites are microporous crystalline aluminosilicates, which belong to the family of the tectosilicates. These materials are constituted by a framework structure composed of TO_4 tetrahedra (T= Si, Al) interconnected through O atoms.[2] For a purely siliceous structure, the combination of TO_4 (T = Si) units leads to silica (SiO_2), with a complete charge balance within the structure.[2] Nevertheless, when Al atoms are incorporated into the silica framework, the +3

charge on the Al makes the zeolite framework negatively charged, due to difference between the $(AlO_4)^{5-}$ and $(SiO_4)^{4-}$ tetrahedral.[2,3] This negative charge requires the presence of inorganic or organic cations within the structure to keep the overall framework neutral[1-3] (Fig. 1).
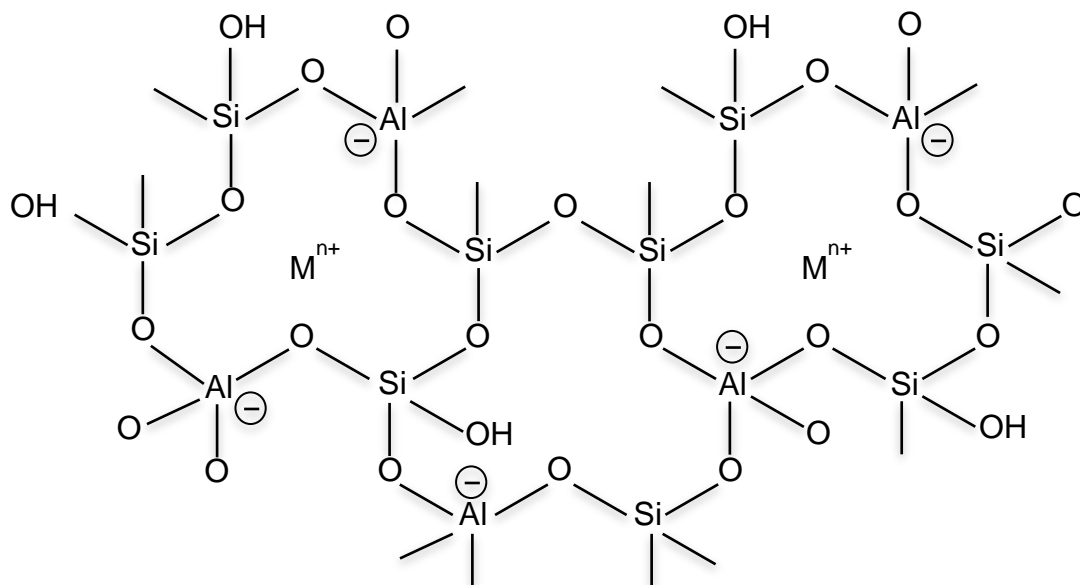

Fig. 1. Two-dimensional representation of the framework structure of zeolites. "Reprinted (adapted) from Ref.[3], Copyright (2006), with permission from Elsevier".

The zeolite structure is made up of three components: the aluminosilicate framework $[Al_xSi_{1-x}O_2]$, extraframework or exchangeable cations $(M_{x/n}^{n+})$ and water (yH_2O). The simplified formula of aluminosilicate zeolites is $M_{x/n}^{n+}[Al_xSi_{1-x}O_2] \cdot yH_2O$, where x can vary from 0-0.5, y represents water molecules and M^{n+} can be either inorganic or organic cation.[2,6] Inorganic cations are usually alkaline or alkaline earth, and organic cations could be alkylammonium. These extraframework cations are ion exchangeable and give rise to the rich ion-exchange chemistry of these materials.[2,3] The water and organic non-

framework cations can be easily removed by a thermal treatment/oxidation, making the intracrystalline space fully accesible.[2]

The amount of Al within the framework can vary over a wide range, with the Si/Al ratio ranging from 1 to ∞.[2] Lowenstein proposed that the lower limit of Si/Al in a zeolite framework of 1 arises because placement of adjacent $(AlO_4)^{5-}$ tetrahedra is not favored because of electrostatic repulsions between negative charges.[2] The framework composition depends on the synthesis conditions. Post-synthesis modifications to insert Si or Al into the framework have also been developed. The composition of zeolites, especially the Si/Al ratio, determines their properties and often is limited by the framework type itself. As the Si/Al ratio of the framework increases, the hydrothermal stability as well as the hydrophobicity increases.[2] Purely siliceous zeolites were reported, although most of them contain Al at ppm or ppb levels.[1] High-silica zeolites present Si/Al ratios higher than 5, although zeolites with Si/Al ratios from 10 to 100 have been reported.[2] Even though the Al content is low, these zeolites manifest acidity. An example of a high-silica zeolite is the synthetic ZSM-5 (ratio Si/Al>15). Intermediate silica zeolites present a Si/Al ratio between 2 and 5. For example, Y zeolite belongs to this group of zeolites.[2] Usually, a larger Al content means greater overall acidity but sometimes it is offset by lowered stability.[1] The Si/Al ratio of low-silica or Al-rich zeolites is less than 2. Most zeolites found in nature are of lower Si/Al ratios such as A and X zeolites (ratios Si/Al between 1.0-1.5). Due to their high Al content, these zeolites have the highest cation contents and are excellent ion-exchange agents.[2]

Tetrahedra are the primary building units of zeolites, but the frameworks can also be considered in terms of secondary building units, which are networks

of tetrahedra linked through oxygen bridges.[6] The combination of tetrahedra in 3D results in a large variety of rings that are responsible for the cages, cavities and pore windows within the framework of the zeolites. Fig. 2 shows two schematic structures of important zeolites and the representation of their primary porous system.
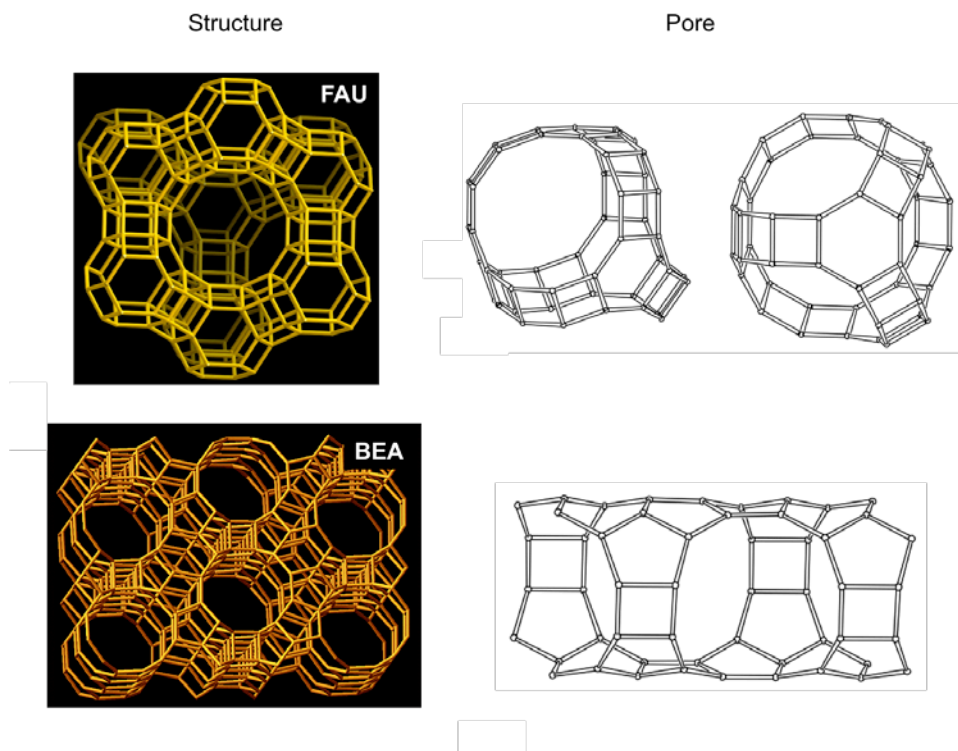
Fig. 2. Schematic structures of the FAU and BEA zeolites, and the representation of their primary pore system. Source: figures obtained from IZA webpage.[5]

Zeolite structures are described in terms of pore size, geometry and connectivity/dimensionality of the pore space.[6] The internal volume of zeolites consists of interconnected cages or channels, which can be from 1D to 3D.[2] The measure of the pore size is in terms of the number ´n´ of T atoms in the circumference of the channel, defined as the ´n-ring´ or nMR.[1] Zeolites with channels or pore openings (windows) described by planar 6MRs or less have

pore sizes around 2 Å, those with planar 8MR windows or channels have pore sizes around 4 Å and are known as small-pore, those with planar 10MR windows or channels as medium-pore (5.5 Å) and those with planar 12MR windows or channels as large-pore (7.5 Å).[6] There are also zeolites with pore openings limited by 14MRs or 18MRs or more, these are known as extra-large-pore solids.[6] Fig. 3 shows pore sizes of different zeolite frameworks.
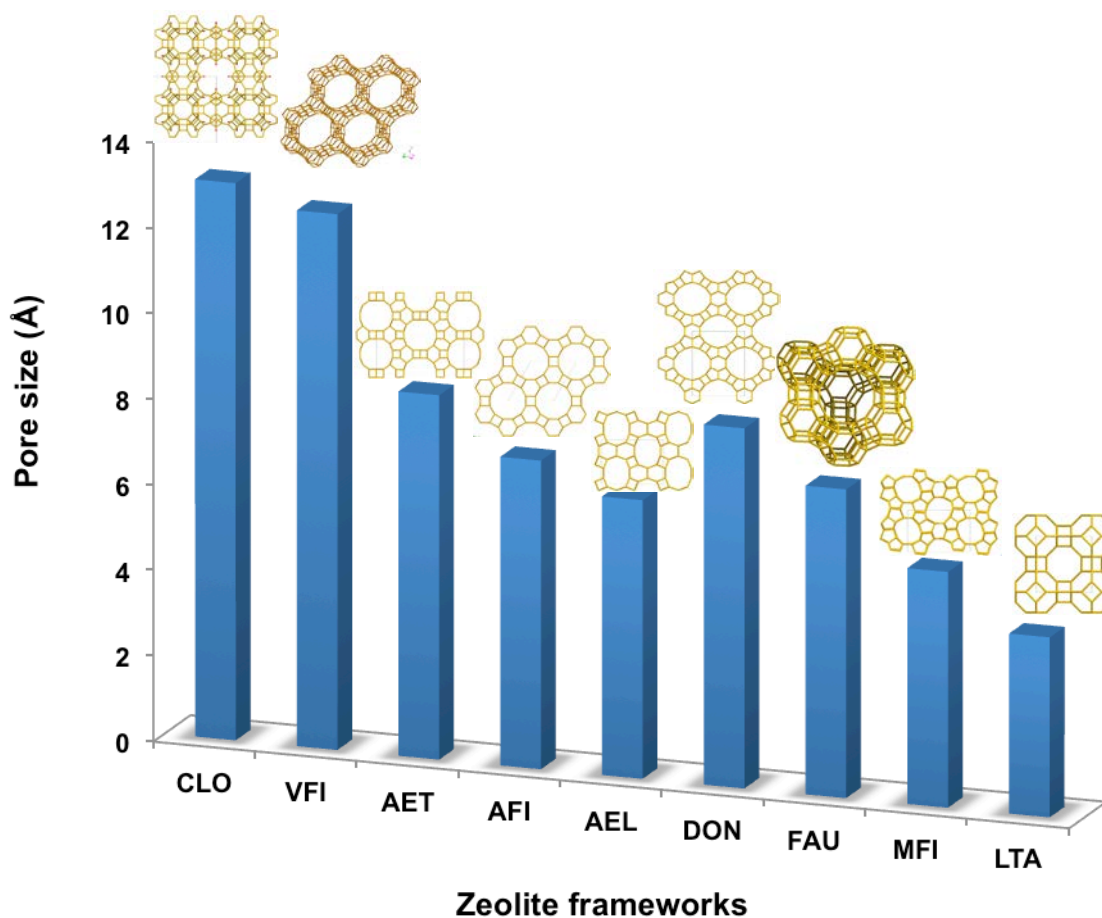

Fig. 3. Comparison of the pore size of different zeolites framework structures. CLO, Cloverite; VFI, VPI-5; AET, AlPO-8; AFI, AlPO-5; AEL, AlPO-11; DON, UTD-1F; FAU, Faujasite; MFI, ZSM-5; LTA, Linde Type A. "Reprinted (adapted) with permission from Ref. [2]. Copyright (2003) American Chemical Society".

10

Natural zeolites possess medium or large pores with low Si/Al ratios, however some of their synthetic analogs were prepared with more silicon, resulting in extra-large pores. Due to the above, zeolites have the capacity to discriminate molecules with dimensional differences less than 1 Å, according to their size and shape. For this reason, zeolites are known as molecular sieves.[2] On the other hand, zeolites present an internal surface, which is highly accessible and can compose more than 98% of the total surface area, being the later around 300-700 $m^2 g^{-1}$. Low-silica zeolites are hydrophilic and unstable in acid, whereas high-silica zeolites are stable in boiling mineral acids, unstable in basic solution and hydrophobic. Thermal stability of zeolites varies according to Si/Al ratio, for low-silica zeolites the decomposition temperature is around 700 °C, whereas for purely siliceous zeolites is approximately 1300 °C.[2] Their catalytic action is due to their strongly acidic nature: the terminal hydroxyl groups in the framework are considered Brönsted-acid sites and the interaction of hydroxyl oxygen with a T atom produces Lewis-acid sites.[3] Cation concentration, siting, and exchange selectivity also depend on Si/Al ratios.[2] Their ability to exchange one cation for another is known as their "cation-exchange capacity" or "CEC". Total CEC in natural zeolites vary from 0.25 to 3 meq g^{-1}.[4]

Zeolites, as described above, are of great interest because their ordered microporous structures combined with high surface area, ion-exchange capacity, thermal and chemical stability, and other beneficial qualities as their low cost of obtaining from natural sources or synthesis, their availability in great amounts and their simple modification to get the desired physical and chemical properties.[3] Additionally, the ability of zeolites to discriminate molecules based

on their size or shape expands the concept of molecular sieving and in more detail the so-called shape selectivity. Therefore, zeolites are of great interest for many applications with significant commercial impact[1-4] in different fields such as catalysis, petrochemistry, environmental remediation and medicine, among others. More specifically, zeolites have been used as selective adsorbents and ion-exchangers for environmental soil remediation, agriculture, horticulture, malodors control, but their primary use has been in water and wastewater treatment of both organic compounds and heavy-metal ions.[3,7] In 2006, Granda Valdés et al.[3] revised some important analytical applications of zeolites mainly in the field of sensors employing zeolite-based electrodes for inorganic and organic compounds determination or sensors to detect gases, and they briefly discussed some works related with separation and preconcentration methodologies.[3] Up to date, the number of publications about applications of zeolites in Analytical Chemistry has increased, but it is still scarce considering the excellent possibilities offered by these materials. Therefore, the aim of this work is reviewing extraction and microextraction techniques such as solid-phase microextraction (SPME), magnetic solid-phase extraction (MSPE) and dispersive solid-phase extraction (DSPE), among others, where zeolites and zeolite-based materials have been used as extractant phases for inorganic and organic compounds determination.

2. Zeolites and zeolite-based materials in extraction and microextraction techniques

Every analytical chemist knows that "*the best sample preparation is the one that does not exist*", however, it is considered a utopia because samples usually

need to be adapted to the measurement instrument.[8] Sample preparation has always been considered the Achilles heel of the analytical procedure due to its drawbacks such as tediousness, high degree of manipulation, risk of losses and contamination, the employment of large amounts of sample, solvents and sorbents, and therefore, generation of large amounts of wastes.[8] For this reason, many efforts in recent decades have been focused on the reduction of this negative impact over the analytical procedure.[8] Nowadays, there are many sample preparation strategies available for these purposes, being solid-phase extraction (SPE)[9] one of the most commonly employed technique for many years. However, this technique presents some of the classical disadvantages of sample preparation such as large volumes of toxic organic solvents and samples, high degrees of sample manipulation and sorbents are limited, among others. For the reasons described above, this technique has been replaced in the last two decades by its miniaturized technique, SPME,[10] maintaining their advantages and reducing or eliminating most of the drawbacks. One of the main limitations of SPE and SPME techniques is the reduced number of sorbents, therefore, zeolites and zeolites-based materials are an excellent alternative to replace the conventional sorbents.

Raw zeolites act mainly as cation-exchange materials, and therefore, the first application in 1999 was focused on the use of a zeolite as extractant material for metals determination.[11] The cation-exchange property mainly depends on the Si/Al ratio, where low ratios favor this kind of interactions. Otherwise, high Si/Al ratios reduce the hydrophilic character and the cation-exchange capacity, allowing the adsorption of organic molecules.[4] However, even at high Si/Al ratios the adsorption of anions or organic molecules is low.

Regarding to this, zeolite adsorption properties can be easily modified through different paths. Firstly, the main modification to increase the extraction of organic molecules is the treatment with surfactants, mainly cationic such as cetyltrimethylammonium bromide, sodium dodecyl sulfate or tetradecyldimethylbenzylammonium chloride, to increase the hydrophobic interactions.[12,13] The modification is easily achieved by exchanging the cation of the zeolite by the cation of the surfactant. Additionally and after the surfactant modification, the zeolite can be further modified with a chelating agent, being immobilized on the cationic surface to increase the metal affinity.[14,15] Another significant modification is the decoration of the zeolites with iron oxide (i.e., Fe_3O_4 or Fe_2O_3) nanoparticles to provide paramagnetic properties.[16–20] Magnetic sorbents are widely used nowadays in (micro)extraction techniques due to the easy handling of the sorbent avoiding filtration or centrifuges for phases separation, doing the extraction procedure more environmentally friendly and portable for on-site extractions. For example, in dispersive (micro)extraction techniques the phases separation is carried out with an external magnetic field (i.e., Neodymium (Nd) magnet).[18,20]

Zeolites commonly used in extraction and microextraction techniques are summarized in Table 1. Zeolites have been used as raw materials or modified mainly with surfactants, chelating agents, metals and/or metallic particles.

14

Table 1. Properties of the most commonly used zeolites in extraction and microextraction techniques.

Zeolite	Chemical formula	IZA code	Channel dimensionality	Pore opening	Pore dimensions/Å	Ref.
Phillipsite	$[K^+_2(Ca^{2+},Na^+_2)_2 (H_2O)_{12}] [Al_6Si_{10} O_{32}]$	PHI	3D	8 x 8 x 8	3.8 x 3.8; 3.0 x 4.3; 3.2 x 3.3	[21,22]
Mordenite	$[Na^+_8 (H_2O)_{24}] [Al_8Si_{40} O_{96}]$	MOR	2D	12 x 8	6.5 x 7.0; 2.6 x 5.7	[11,23]
Clinoptilolite	$[Ca^{2+}_4 (H_2O)_{24}][Al_8Si_{28}O_{72}]$	HEU	2D	10 x 8	3.1 x 5.5 + 4.1 x 4.1; 2.8 x 3.4	[16,24–34]
ZSM-5	$[Na^+_n (H_2O)_{16}] [Al_nSi_{96-n} O_{192}]$, n < 27	MFI	3D	10 x 10	5.1 x 5.5; 5.3 x 5.6	[17,18,20,35,36]
L	$[K^+_6Na^+_3 (H_2O)_{21}] [Al_9Si_{27} O_{72}]$	LTL	3D	12	7.1 x 7.1	[37]
X	$[(Ca^{2+},Mg^{2+}Na^+_2)_{29} (H_2O)_{240}] [Al_{58}Si_{134} O_{384}]$	FAU	3D	12	7.4 x 7.4	[38–40]
Analcime	$[Na^+_{16} (H_2O)_{16}] [Al_{16}Si_{32} O_{96}]$	ANA	3D	-	-	[14,15,41–46]
Y	$[(Ca^{2+},Mg^{2+}Na^+_2)_{29} (H_2O)_{240}] [Al_{58}Si_{134} O_{384}]$	FAU	3D	12	7.4 x 7.4	[13,19,47–51]
Natrolite	$[Na^+_{16} (H_2O)_{16}] [Al_{16}Si_{24} O_{80}]$	NAT	3D	9 x 8	2.5 x 4.1; 2.6 x 3.9	[46,52]
A	$[Na^+_{12} (H_2O)_{27}]_8 [Al_{12}Si_{12} O_{48}]_8$	LTA	3D	8	4.1 x 4.1	[35,40,51,53]
Beta	$[Na^+_7] [Al_7Si_{57} O_{128}]$	BEA	3D	12 x 12	6.6 x 6.7; 5.6 x 5.6	[54–57]

The review has been organized based on the use of zeolites and zeolite-based materials for the extraction of organic (Section 3) or inorganic compounds (Section 4). Both Sections are divided in the different extraction and/or microextraction techniques that employ these materials as extractant phases (Fig. 4). As shown in Fig. 4, the extractant phase configurations available for the extraction of organic compounds are more diverse than those employed for metals extraction.
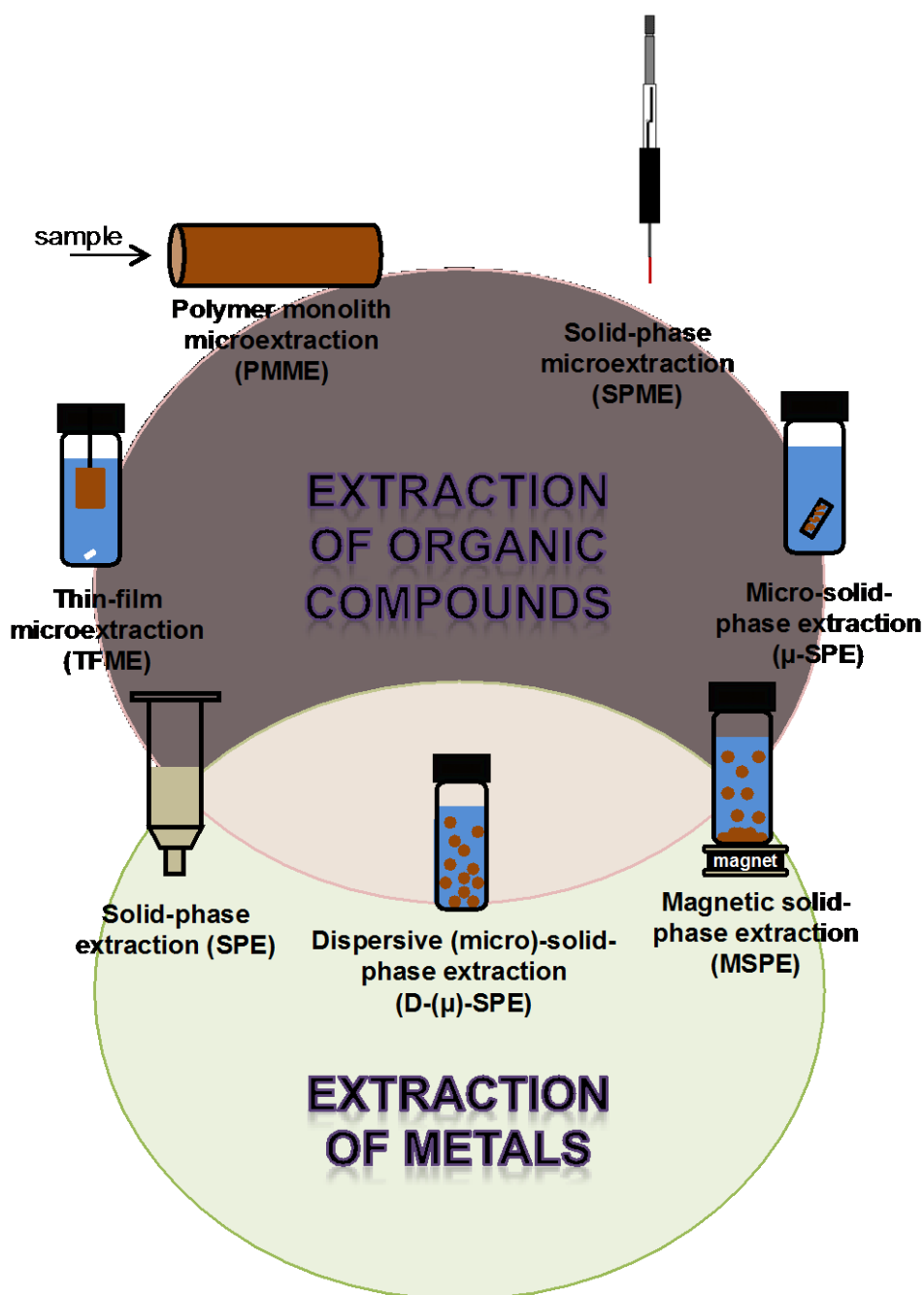
Fig. 4. Scheme of the extraction and microextraction techniques that employ zeolites or zeolite-based materials for the extraction of organic compounds and metals.

3. Extraction of organic compounds

Solid-phase extraction and microextraction techniques are widely employed in sample preparation providing analyte isolation, preconcentration and sample clean-up.[9] The study of different sorbents that improve extraction yields and selectivity towards target analytes has been a recurrent issue in numerous publications.[58–62] Among the proposed sorbents (e.g., ionic liquids, molecularly imprinted polymers, carbon nanomaterials), zeolites have been presented as a valuable alternative to separate and preconcentrate organic analytes from different matrices prior to instrumental analysis. Table 2 summarizes the analytical methods discussed in this section based on the extraction of organic compounds using zeolites and zeolite-based materials as sorbents.

Table 2. Extraction of organic compounds using zeolite and zeolite-based materials as sorbents.

Sorbent	Analyte	Sample	Extraction technique: conditions	Separation/detection technique	LOD (μg L^{-1})	Ref.
Microemulsion modified natural zeolite (major mineral: phillipsite, minor mineral: fassaite)	Sulphonated and azo sulphonated dyes	Textil wastewater	SPE: polyethylene column packed with 1 g of modified zeolite, 100-250 mL of sample at pH=7, elution with 5 mL methanol/water (70:30 v/v)	UV-vis spectrophotometry	15-25[a]	21
Natural zeolite (major mineral: phillipsite, minor mineral: fassaite)	Cationic dyes	Stream water	SPE: polyethylene tube packed with 0.3 g of zeolite, 1 L of sample at pH=5, elution with 10 mL 0.02 M HNO$_3$	UV-vis spectrophotometry	43-245[b]	22
CTA modified NaY zeolite	Carbamate pesticides	Rice filed, underground, tap and waste water	SPE: cartridge packed with 100 mg of zeolite, on-line modification with CTA, extraction 20 mL of sample, elution with 750 μL of methanol	LC-UV	0.005-140[c]	13
AChE-immobilized beta zeolite	AChE binders	Crude extract of *Corydalis yanhusuo*	SPE: sample solution incubated with 0.025 mg AChE modified zeolite at 37 ºC for 20 min, elution with 20 mL of 50% (v/v) methanol/water	UPLC-Q-TOF-MS	293[c]	54
Natural clinoptilolite, TMA and ODTMA modified natural clinoptilolites	Zearalenone	Beer	DSPE: 200 mg of sorbent, 100 mL of sample at pH=4.3, extraction for 30 min, filtration, elution with 5 mL of ethanol for 30 min	LC-FD	20[d]	24
PANI modified NaY zeolite	Pesticides	Fruits, vegetables and water	DSPE: 150 mg of sorbent in 125 mL sample (pH=8), extraction for 4 min, transfering the sorbent to a SPE elution column, removing interferences with water, elution of analytes with 3 mL of 0.01 M NaOH in 90% acetonitrile	HPLC-PDA	1-1000[c]	47
Natural zeolite	Ketonic bodies	Urine	SPME: HS mode, 5 mL of sample at 30 ºC, extraction for 15 min, thermal desorption at 250 ºC	GC-FID	300-600[c]	63
Natural zeolite	BTEX	Water and soil	SPME: HS mode, 10 mL of water samples at 25 ºC or 2 g of soil samples sonicated at 40 º C, extraction for 30 min (water samples) or 25 min (soil samples), thermal desorption at 250 ºC	GC-FID	0.66-1.66[c]	64
LTA zeolite *vs* ZSM-5 zeolite	Organophosphate neurotoxins	Sea and river water and synthetic urine	SPME: DI mode, 10 μL of rain water (pH=6), seawater (pH=8) and synthetic urine (pH=6), extraction for 1 min	Low temperature plasma MS	24.46-98.89[a]	35
LTL zeolite	Ochratoxin A	Coffee and cereal	μ-SPE: 25 mg packed zeolite, 10 mL of sample at pH=1.5, extraction for 40 min, elution with 400 μL of methanol	LC-FD	0.03-0.09[a] (ng g^{-1})	37
ZSM-5/Tenax TA	VOCs	Aqueous standards	TFME: HS and DI modes, 15 mL of sample at RT, extraction for 30 min, thermal desorption at 220 ºC with He stream	GC-MS	12[e] (benzene) 13[e] (toluene)	36

Sorbent	Analyte	Sample	Extraction conditions	Detection	LOD	Ref
Synthetic zeolite	Synthetic colorants	Red lipsticks	PMME: 5 mg of modified zeolite, 1.2 mL of sample at pH=3, elution with 0.5% ammonia solution/methanol (1:1, v/v)	LC-MWD	1.3-3.7[c]	65
Lantanum(III) modified natural clinoptilolite	Hemoglobin	Blood	D-μ-SPE: 10 mg of sorbent, 500 μL of sample at pH=5, extraction for 30 min, centrifugation for 5 min at 2000 rpm, elution with 500 μL of 0.01 M Na_3PO_4 for 10 min	SDS-PAGE	-[f]	25
Natural mordenite	Creatinine	PBS and PBS with albumin solutions	D-μ-SPE: 2 mL of sample/40 mg of sorbent, extraction for 12 h at 37 ºC, centrifugation, drying of solid sorbent at 37 ºC for 1 h	DR-UV	-[f]	66
BEA zeolite	PAHs	Tap and lake water	D-μ-SPE: 2 mg of zeolite, 1 mL of sample, extraction for 1 min, centrifugation for 5 min at 13400 rpm, elution with 100 μL of methanol/water (70:30, v/v) for 5 min	LC-UV/FD	0.0011-0.0499[a]	55
BEA zeolite	PAHs	Tap and lake water	D-μ-SPE: 2 mg of zeolite, 1 mL of sample, extraction for 1 min, centrifugation for 5 min at 13400 rpm, elution with 100 μL of methanol/water (70:30, v/v) for 5 min, addition of 100 μL of octane	LETRSS	0.0011-0.194[a]	56
CTA modified NaY zeolite	Carbamate pesticides	Fruits, vegetables and surface water	D-μ-SPE: 40 mg of sorbent, 7 mL of sample, vortex-assisted extraction for 2 min, filtration, elution with 500 μL of methanol	LC-PDA	0.004-4.000[c] (mg Kg^{-1})	48
Natural clinoptilolite/Fe_3O_4	Phthalates	Mineral water	MSPE: 80 mg of sorbent, 10 mL of sample, vortex-assisted extraction for 16 min, elution with 4 mL of acetone for 8 min	GC-FID	2.80-3.20[d]	16
CC[4]A modified magnetic ZSM-5 zeolite	Phenolic antioxidants	Juice and infant milk powder	MSPE: 30 mg of sorbent, 100 mL of sample at pH=3, ultrasound-assisted extraction for 10 min, elution with 1 mL of methanol	LC-UV	6.0-67.5[a]	17
ZSM-5/iron oxide	BTEX	Industrial wastewater, drinking and river water	MSPE: 138 mg of sorbent, 22 mL of sample, manual agitation for 11 min, elution with 0.5 mL of acetone for 5 min	GC-MS	0.3-3[a]	18
Hydrophobic silica zeolite	BTX	Indoor air	Passive sampling in controlled atmosphere and real environments, thermal desorption at 300 ºC for 30 min	GC-MS	6.1-11[g] (μg m^{-3} for 24 h exposure)	67
NaX zeolite	Oxygenated solvents	Fire debris	Heated passive HS extraction, desorption with 500 μL of methyl ethyl ketone	GC-MS	-[f]	39
NaX zeolite and activated charcoal	Oxygenated solvents and petroleum derivatives	Fire debris	Heated passive HS extraction, desorption with methanol (zeolite) or CS_2 (charcoal)	GC-MS	-[f]	38

LOD, limit of detection; SPE, solid-phase extraction; UV-vis, ultraviolet-visible; CTA, cetyltrimethylammonium; LC-UV, liquid chromatography-ultraviolet detection; AChE, acetylcholinesterase; UPLC-Q-TOF-MS, ultra-high performance liquid chromatography-quadrupole time-of-flight mass spectrometry; TMA, tetramethylammonium; ODTMA, octadecyltrimethylammonium; DSPE, dispersive solid-phase extraction; LC-FD, liquid chromatography-fluorescence detection; PANI, polyaniline; HPLC-PDA, high-performance liquid chromatography-photodiode array detection; SPME, solid-phase microextraction; HS, headspace; GC-FID, gas chromatography-flame ionization detection; BTEX, benzene, toluene, ethylbenzene and xylenes; LTA, Linde Type A; ZSM-5, Zeolite Socony Mobil–5; DI, direct immersion; MS, mass spectrometry; LTL, Linde Type L; μ-SPE, micro-solid-phase extraction; VOCs, volatile organic compounds; TFME, thin-film microextraction; RT, room-temperature;

GC-MS, gas chromatography-mass spectrometry; PMME, polymer monolith microextraction; LC-MWD, liquid chromatography-multiple wavelength detection; D-µ-SPE, dispersive micro-solid-phase extraction; SDS-PAGE, sodium dodecyl sulfate-polyacrylamide gel electrophoresis; PBS, phosphate buffered saline; DR-UV, diffuse reflectance ultraviolet; BEA, beta polymorph A; PAHs, polycyclic aromatic hydrocarbons; LC-UV/FD, liquid chromatography-ultraviolet/fluorescence detection; LETRSS, laser-excited time-resolved Shpol´skii spectroscopy; LC-PDA, liquid chromatography-photodiode array detection; MSPE, magnetic solid-phase extraction; CC[4]A, carboxylatocalix[4]arenes; BTX, benzene, toluene and xylenes.

[a] Calculated using $3s_{blank}/m$, where s_{blank} is the standard deviation of blank and m is a slope of the calibration curve.

[b] Estimated using Lorber´s method.

[c] Calculated as three times signal-to-noise ratio.

[d] LOD calculation not mentioned.

[e] Calculated from the calibration curve cross section for a blank signal.

[f] LOD not mentioned by the authors.

[g] Calculated as $t_{(n-1,1-\alpha=0.99)}\sigma$, where t is the student's t-value for n-1 degrees of freedom at 99% confidence level, and σ is the standard deviation of six blank samplers.

3.1. Solid-phase extraction

Typically, solid-phase extraction (SPE) consists of cartridges or columns packed with sorbent where the analyte is retained when liquid samples flow through it.[9] Then, a proper solvent is employed to elute and recover the analyte for further determination.[9] Al-Degs et al.[21] modified a natural zeolite with a microemulsion for the SPE of sulphonated and azo sulphonated dyes from textile wastewater. The microemulsion was based on saponified coconut oil (surfactant), isoamyl alcohol (cosurfactant) and oil phase. The natural zeolite was modified by simply mixing it with the already prepared microemulsion and a final drying step. For SPE, sample solution was passed through a polyethylene column packed with the modified zeolite and then, adsorbed analytes were eluted using a mixture of methanol/water. Thereafter, the concentration of five dyes was determined spectrophotometrically without previous chromatographic separation, using multivariate calibration. It was demonstrated that the microemulsion played a key role in the extraction process since the modified zeolite provided higher enrichment factors than the unmodified zeolite[21]. In addition, the limits of detection (LODs) obtained with the proposed method were similar to those obtained with other sorbents (e.g., C_{18} columns) and more complex analytical instrumentation (e.g., liquid chromatography-atmospheric pressure ionization mass spectrometry).[21] In a later publication, the same research group carried out a comparative study about different sorbents (i.e., activated carbon, natural diatomite and natural zeolite) for the SPE of cationic dyes from water samples.[22] After extraction with the corresponding packed sorbent and elution with a HNO_3 solution, five dyes were simultaneously determined by spectrophotometry using multivariate calibration.[22] Results

revealed a better performance of diatomite compared to zeolite and the lowest extraction yields were obtained with activated carbon, probably due to stronger interactions with analytes that hindered their release during elution.[22]

The adsorption and desorption of carbamate pesticides in different surfactant-modified sorbents, namely: silica and NaY zeolite coated with cetyltrimethylammonium bromide (CTA-Br) and alumina coated with sodium dodecyl sulfate, was investigated by Arnnok et al.[12] in a preliminary work for comparative purposes. On one hand, results showed that some pesticides could be adsorbed onto the raw materials (i.e., silica, NaY zeolite and alumina). However, enhancement in sorption of less polar compounds was observed using surfactant-modified sorbents due to the presence of an organic environment of major affinity.[12] On the other hand, desorption studies using methanol revealed that the analytes release from surfactant-modified sorbents was better than from the unmodified ones. Finally, CTA modified NaY zeolite was selected as the best candidate to act as sorbent for the SPE of carbamate pesticides.[12] Next, carbamate pesticides were determined in environmental water samples using a flow system that included the on-line zeolite modification with CTA-Br, analytes retention, elution and determination by liquid chromatography-ultraviolet detection (LC-UV).[13] Although the LODs obtained were generally higher than those obtained in previous publications using commercial sorbents (e.g., C_{18}), they were low enough to satisfy the current normative about maximum contaminant limits.[13] In addition, the proposed on-line method introduced benefits related to less sample manipulation, short analysis time and low solvent consumption.[13]

A new zeolite-based SPE has been recently proposed by Tao et al.[54] for the extraction of acetylcholinesterase (AChE) binders from crude extract of *Corydalis yanhusuo*. In a 1.5 mL centrifuge tube, sample solution was incubated with 0.025 mg AChE modified zeolite at 37 ºC for 20 min. Thereafter, AChE-immobilized zeolite was washed using methanol/water to dissociate specific bound compounds (i.e., AChE binders). Authors named the proposed extraction method as SPE, however the sorbent was not packed within a cartridge or a column, and the described procedure could be more alike other extraction techniques (e.g., dispersive micro-solid-phase extraction). During initial experiments, Y, ZSM-5 and beta zeolites were modified with AChE obtaining the largest percentage of adsorbed AChE and, therefore, the highest extraction capacity by using beta zeolite. In addition, reusability tests proved that the activity of AChE immobilized zeolite was 89% after 10 cycles, thus providing the advantages of reduced test costs and increased experimental throughput.

Finally, it should be mentioned one publication in which a column loaded with Y zeolite was employed to remove interfering species from the target analyte (i.e., morphine) in plasma samples.[68] In a previous step, plasma samples were subjected to liquid-phase extraction using tetrahydrofuran as extractant solvent. Then, the extractant phase was passed through the zeolite-based column where unknown compounds (i.e., interferences) were effectively retained and separated from morphine. Thereby, overlapped peaks that initially appeared in the final chromatographic analysis were avoided.

3.2. Dispersive solid-phase extraction

In dispersive solid-phase extraction (DSPE), the solid sorbent is directly introduced and dispersed into the sample solution increasing active surface area and, thereby, enhancing extraction kinetics.[69] After extraction, extractant phase is normally separated by centrifugation or filtration. Then, analytes can be determined directly on the solid or eluted for the subsequent analysis of the eluated phase.[69] Pansinli and Henden[24] investigated natural clinoptilolite and clinoptilolite modified with tetramethylammonium bromide (TMA-Br) or octadecyltrimethylammonium bromide (ODTMA-Br) for the DSPE of zearalenone from beer samples. The studied sorbents were mixed with degassed beer samples and shaken until sorption equilibrium conditions. Later, the mixture was filtrated, sorbent was washed and ethanol was finally added to the solid to elute the analyte. Finally, the ethanol phase was analyzed by liquid chromatography-fluorescence detection (LC-FD). The possibility of reusing the zeolite-based sorbents was investigated, concluding that the three zeolites (i.e., natural clinoptilolite and clinoptilolite modified with TMA-Br or ODTMA-Br) were suitable for six repetitive uses, although a cleaning step for 30 min with 10 mL of ethanol was necessary between extractions. In the analysis of real samples, low recoveries (i.e., 44-57%) were obtained using the natural and TMA modified clinoptilolite. On the contrary, recovery reached 90% with ODTMA modified clinoptilolite showing the effective use of this sorbent to preconcentrate zearalenone from beer samples, probably due to an increase in the hydrophobicity of the zeolite surface.[24]

Polyaniline (PANI) modified NaY zeolite has been investigated by Arnnok et al.[47] for the extraction of multi-class pesticides from environmental and food

samples. The modified sorbent was obtained via oxidative polymerization of aniline onto the surface of the NaY zeolite. PANI form can be varied depending on acidity (protonation/deprotonation), thus, various pH conditions were tested during the synthesis and the resulting modified sorbents were evaluated in order to achieve the highest pesticide sorption capacity. PANI modified NaY zeolite obtained under strong acidic conditions (pH 1-2) exhibited the best performance upon extraction.[47] During scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) analysis, sodium ions and aluminium atoms were not detected on the surface of PANI modified NaY zeolite. This fact revealed that ion exchange between sodium ions on the zeolite surface and anilinium ions occurred during polymerization and, consequently, the zeolite surface was almost completely covered with PANI.[47] For DSPE, PANI modified NaY zeolite was added to 125 mL of sample and mechanically shaken to allow sorption of the pesticides onto the sorbent. After that, the suspension was transferred to a polypropylene syringe column serving as a SPE eluting column. Polar interferences (e.g., sugars, salts) were removed with water and, finally, analytes were eluted using a solution of 0.01 M NaOH in 90% acetonitrile. Authors compared the capability of PANI modified NaY zeolite for the determination of multi-class pesticides with a commercial C_{18} sorbent obtaining comparable results, but highlighting the low cost of the proposed sorbent.[47]

All the above mentioned methods employed large amounts of sorbent, solvents and sample (see Table 2), as well as long extraction times. As alternative, new microextraction techniques using zeolites and zeolite-based

materials as extractant phase were developed, trying to overcome such disadvantages inherent to SPE and DSPE.

3.3. Solid-phase microextraction

Solid-phase microextraction (SPME) is based on the extraction of analytes into a fused silica fiber coated with a proper sorbent polymer.[10,70,71] After extraction in direct immersion (DI) or headspace (HS) modes, analytes are chemically (with low solvent volumes) or thermally desorbed for subsequent determination. Matin et al.[63] proposed a new SPME fiber based on activated carbon and natural zeolite for the extraction of ketone bodies from urine samples. The extraction of acetone, acetoacetate and β-hydroxybutyrate was carried out in the HS mode. Then, analytes were thermally desorbed and determined by gas chromatography-flame ionization detection (GC-FID)[63]. The proposed fiber showed a high durability and better performance than fibers based exclusively on activated carbon or zeolite.[63] Other new SPME fiber coated with zeolite and SiC was presented for the preconcentration of benzene, toluene, ethylbenzene and xylenes (BTEX) from water and soil samples.[64] During the extraction, the fiber was disposed in the HS of stirred water samples or sonicated soil samples. Then, the fiber was immediately inserted in the hot injection port of a GC-FID system for thermal desorption and ensuing analysis. Different fiber compositions (i.e., SiC/zeolite weight ratios) were evaluated. Results showed that coating made of 20% SiC and 80% zeolite possessed the maximum ability for BTEX extraction due to a synergic combination of the adsorption capacity of zeolite and porosity given by SiC.[64] Finally, a recent publication reported a comparative study of two different zeolite-based coatings

(i.e., LTA and ZSM-5) in a new method whereby SPME was directly coupled to low temperature plasma mass spectrometry to determine organophosphate neurotoxins in water and urine samples.[35] The SPME fibers consisted of a stainless steel needle coated with LTA or ZSM-5 zeolites, respectively. After the SPME in DI mode, the extraction unit was directly inserted into a low temperature plasma ionization chamber and served as ionization electrode (i.e., ionization source). The effect of a pre-conditioning step of the SPME fibers with different cations (i.e., Na^+ and Cu^{2+}) was investigated and results showed that the presence of Cu^{2+} ions improved extraction yields probably due to strong Cu^{2+}-phosphonate interactions.[35] Finally, LTA zeolite showed better extraction performance due to higher density of cation-exchange sites compared to ZSM-5 and, therefore, more sites for the coordination and preconcentration of organophosphate analytes.[35]

All the SPME methods included in this section carried out the thermal desorption or direct determination of analytes after extraction, thereby avoiding time-consuming elution steps and reducing solvents consumption. On the contrary, as major inconvenients it could be mentioned the well-known fibers fragility and pre-conditioning steps.

3.4. Micro-solid-phase extraction

In micro-solid-phase extraction (μ-SPE), a small bag of porous membrane is filled with the sorbent and directly submerged into sample solution.[71] Lee et al.[37] proposed Linde Type L (LTL) zeolite as new sorbent for the μ-SPE of ochratoxin A from coffee and cereal samples. Solid samples were previously mixed with a $NaHCO_3$ solution, shaken and filtrated. Then, the μ-

SPE device (i.e., zeolite packed inside a polypropylene membrane) was placed in stirred sample filtrates. After extraction, the device was retrieved, washed, dried and deposited in a small vial for analyte desorption with methanol. Finally, methanol phase was analyzed by LC-FD. LTL zeolites with different morphologies (i.e., nanosized, rods, cylinders and needles) were evaluated obtaining the best extraction yield for LTL zeolite in the form of cylinders. Authors associated these results with the existence of a higher number of accessible channels with longer lengths where the analyte could enter deeper and be trapped more effectively.[37] Moreover, cylinders of LTL zeolite showed equal or greater extraction efficiency than molecularly imprinted polymers and commonly used C_8, C_{18} and C_{30} sorbents,[37] with the undoubted advantage of being a low cost and widely available material.

3.5. Thin-film microextraction

In thin-film microextraction (TFME), a sheet of flat film with a high surface area-to-volume ratio is used as the extraction phase.[70] Goda et al.[36] proposed a novel TFME device based on ZSM-5 zeolite and Tenax TA porous polymer in order to preconcentrate acetone, hexane, cyclohexane, dichloromethane, diethyl ether, benzene, toluene, benzaldehyde, 1-pentanol and 1-octanol from water. Zeolite and Tenax TA were sequentially deposited on an aluminium support by dip-coating. The adsorption device was employed in both HS and DI extraction modes. After extraction, analytes were thermally desorbed for final determination by gas chromatography-mass spectrometry (GC-MS). Comparing the extraction performance of ZSM-5/Tenax TA and Tenax TA coatings allowed concluding that only some analytes (i.e., hexane, cyclohexane,

dichloromethane, benzene and toluene) were better extracted with the hybrid material. Therefore, the proposed zeolite-based sorbent showed certain selectivity within tested analytes. Finally, authors pointed out the presence of unexpected peaks in the GC-MS chromatogram. These peaks were assigned to hydrocarbons and benzene derivatives coming from the thermal degradation of adsorbed compounds due to the well-known catalytic activity of ZSM-5 zeolite.[36] Authors did not discuss the selection of ZMS-5 as sorbent, although the use of an alternative zeolite could have avoided degradation problems and improved analytical performance.

3.6. Polymer monolith microextraction

Polymer monolith microextraction (PMME) was introduced as an alternative to SPME in order to improve extraction process using high surface area polymer monoliths inside capillary columns.[65] For the first time, Wang et al.[65] presented the modification of a poly(methacrylic acid-ethylene dimethacrylate) column with synthetic zeolite for the extraction of seven colorants from red lipsticks. Lipsticks were dissolved in dimethyl sulfoxide and filtered before PMME. Then, sample solution was passed through the modified polymer monolithic column and eluted with an ammonia solution/methanol mixture for subsequent analysis by liquid chromatography-multiple wavelength detection.[65] Zeolite modified polymer monolith was characterized by different techniques (e.g., scanning electron microscopy and thermogravimetry) showing high porous structure and thermal stability.[65] In addition, a comparative study about the preconcentration ability of modified and unmodified polymer was

conducted revealing a remarkable enhancement of analytical signal after the extraction with the proposed modified material.[65]

3.7. Dispersive micro-solid-phase extraction

Dispersive micro-solid-phase extraction (D-μ-SPE) is based on the same general procedure above described for DSPE, but employing lower amounts of sorbent (i.e., ≤100 mg sorbent) and sample volume.[69,71] Therefore, D-μ-SPE has been reported as the miniaturized mode of DSPE. A lanthanum(III) modified clinoptilolite was employed for the D-μ-SPE of hemoglobin from blood samples.[25] To modify clinoptilolite, the zeolite was merely mixed with a $La(NO_3)_3$ solution at 100 ºC for 2.5 h. Before extraction, blood samples were diluted and erythrocytes were broken to release hemoglobin. Then, lanthanum(III) modified clinoptilolite was mixed with sample solution and, after extraction and centrifugation, the supernatant was retrieved and a Na_3PO_4 solution was added to desorb the analyte from the lanthanum(III) modified clinoptilolite. The final acceptor phase (i.e., Na_3PO_4 solution) was analyzed by sodium dodecyl sulfate-polyacrylamide gel electrophoresis. Lanthanum(III) possesses high affinity to proteins due to its ability to coordinate with oxygen, aliphatic nitrogen and phosphor ligands.[25] In addition, no adsorption was observed with pure clinoptilolite showing that the affinity of lanthanum(III) with hemoglobin was the responsible force of the extraction process. Therefore, in this work zeolite was basically employed as solid support considering its easy and reproducible modification with lanthanum(III).

Bergé-Lefranc et al.[66] employed mordenite for the D-μ-SPE of creatinine from physiological solutions. Authors had previously studied the adsorption of

creatinine onto mordenite, showing a good extraction performance under physiological conditions.[23] For D-μ-SPE, sample and sorbent were mixed until equilibrium conditions and then, phases were separated by centrifugation. During initial studies, creatinine was determined in the supernatant phase using liquid chromatography-diode array detection or a spectrophotometric method based on the Jaffé reaction.[66] However, diffuse reflectance ultraviolet (DR-UV) spectroscopy measurements were performed directly on the solid phase for the final analytical quantification of the adsorbed creatinine.[66] Thus, the combination of zeolite-based D-μ-SPE with DR-UV is an interesting and promising alternative to those classical procedures that include a desorption step followed by a time-consuming chromatographic technique. However, the advantages of combining zeolite-based D-μ-SPE with DR-UV were partially restricted in the proposed method since 12 h of extraction time were necessary to carried out extractions under equilibrium conditions.

In a preliminary publication, Costa et al.[72] compared the physicochemical properties and extraction performance of different zeolites, namely: BEA, USY and ZSM-5, using polycyclic aromatic hydrocarbons (PAHs) as target analytes. During such studies, BEA showed the greatest efficiencies and, considering the lager external surface area, authors suggested that the adsorption of PAHs predominantly occurred on the external surface of zeolites.[72] Thereafter, authors applied these results in two subsequent publications in which BEA was employed for PAHs determination in water samples using liquid chromatography-ultraviolet/fluorescence detection (LC-UV/FD)[55] or laser-excited time-resolved Shpol´skii spectroscopy[56], respectively. Briefly, BEA was added to water samples and the mixture was shaken. After centrifugation, the

supernatant was removed and methanol/water was added for analytes desorption.[55,56] Lower LODs were obtained with LC-UV/FD for the fifteen PAHs studied. Nevertheless, the method including Shpol´skii spectroscopy also met regulation requirements (i.e., LODs lower than maximum concentration levels stipulated by the Environmental Protection Agency) and, at the same time, time-consuming chromatographic separation was avoided, thus reducing analysis time and the consumption of organic solvents.

Recently, a novel method based on vortex-assisted D-µ-SPE using CTA modified NaY zeolite as sorbent was proposed by Salisaeng et al.[48] to determine carbamate pesticides in fruit, vegetables and water samples. Food samples were previously extracted with an acetic acid/methanol mixture. The extractant phase was evaporated to dryness and the final residue was reconstituted with water. For D-µ-SPE, CTA modified NaY zeolite was added to aqueous solution and vortex-mixed. After that, the mixture was filtered and carbamate pesticides adsorbed on the solid sorbent were eluted with methanol for subsequent determination by liquid chromatography-photodiode array detection.[48] The zeolite-based sorbent used in this work had been previously employed in two above mentioned publications of the same research group.[12,13] Nevertheless, D-µ-SPE technique introduced remarkable advantages as shorter extraction times, less consumption of sorbent and an easier to handle procedure than SPE.

3.8. Magnetic solid-phase extraction

Recently, magnetic solid-phase extraction (MSPE) has received great interest since it facilitates sorbent manipulation.[71] In MSPE, the magnetic sorbent is dispersed into the aqueous phase, normally by vortex agitation[16], ultrasound energy[17] or manual agitation[18]. After extraction, the sorbent is easily separated from the sample solution by applying an external magnetic field (e.g., with a Nd magnet). Therefore, time-consuming filtration or centrifugation steps for phase separation are avoided. Next, target analytes can be desorbed using a proper eluent solvent or temperature for further determination.[71]

Clinoptilolite/Fe_3O_4 composite was recently proposed as a new sorbent for MSPE.[16] In this work, phthalates were determined at trace levels in aqueous samples by GC-FID after extraction with natural clinoptilolite loaded on Fe_3O_4 nanoparticles.[16] Magnetic nanoparticles were synthesized by Fe electrooxidation in a tetramethylammonium chloride (TMA-Cl) solution. Then, the composite was obtained by simply mixing the zeolite with Fe_3O_4 nanoparticles in a thermostatic bath at 90 ºC. BET surface area, pore size and pore volume were evaluated in pure clinoptilolite and clinoptilolite/Fe_3O_4 composite. Results revealed an increase in surface area and pore volume, but a decrease in average pore diameter in the presence of Fe_3O_4. Considering these results, authors concluded that magnetic nanoparticles were disposed on the zeolite surface forming secondary pores.[16] Finally, the comparison of the proposed method (i.e., dynamic linear range, LOD, repeatability) with others methods including MSPE with different sorbent materials (e.g., C_{18}/Fe_3O_4) showed comparable or better results.[16]

Other publication presented the preconcentration of phenolic antioxidants with magnetic ZSM-5 zeolite derived with carboxylatocalix[4]arenes (CC[4]A).[17] The magnetic zeolite was synthesized from SiO_2 gel, $Fe(NO_3)_3$ and $NaAlO_2$ solutions. Afterwards, it was amine functionalized and finally derived with CC[4]A. MSPE was applied to preconcentrate phenolic antioxidants from juice and milk powder samples prior to LC-UV. Authors demonstrated the more efficient preconcentration capacity of magnetic ZSM-5 zeolite derived with CC[4]A compared to magnetic ZSM-5 without derivatization. In addition, LODs were generally lower than those obtained in previous publications using different preconcentration methods (e.g., cloud point extraction, liquid-liquid extraction).[17]

Finally, our research group proposed a new composite based on ZSM-5 zeolite decorated with iron oxide magnetic nanoparticles as a valuable sorbent for MSPE. BTEX were proposed as model analytes and were determined in water samples by GC-MS. The magnetic composite was prepared by precipitation of Fe_2O_3 nanoparticles onto ZSM-5 zeolite. Nitrogen adsorption isotherms revealed a decrease in BET surface area and micropore volume due to the presence of magnetic nanoparticles. The proposed sorbent could be reused in at least twelve consecutive extractions.[18] Finally, good extraction efficiencies were obtained for benzene, toluene and ethylbenzene. However, no preconcentration was obtained for o-xylene isomer probably due to a sterically hindered extraction.[18]

3.9. Passive sampling

Besides SPE and miniaturized SPE techniques, zeolites have also been proposed as sorbents in passive sampling devices.[38,39,67] These devices are used for continuous monitoring of pollutants in environmental matrices, giving interesting information about long-term exposure and time-weighted average concentrations.[67] In recent years, the popularity of passive sampling has increased since it combines sample collection, purification and concentration into a single step. In addition, passive sampling eliminates power supply, being cheaper and more environmentally friendly than active sampling.[67] Du et al.[67] employed a hydrophobic silica zeolite as sorbent to monitor indoor exposure to benzene, toluene and xylenes (BTX) by passive diffuse sampling. BTX determination was performed by GC-MS after thermal desorption. The proposed device was validated under real environmental conditions giving good results at lower cost than other passive samplers.[67] Other publication reported the use of 13X (NaX) zeolite in heated passive HS extraction of oxygenated solvents (ignitable liquids in incendiary fires) from fire debris samples.[39] The high hydrophilic character, pore diameter and available surface area of zeolite made it suitable for the extraction of small polar molecules such as acetone, methanol, ethanol or isopropanol. After extraction, target molecules were desorbed with methyl ethyl ketone and determined by GC-MS.[39] The proposed passive sampler improved the recovery of oxygenated solvents under study in comparison to the commonly used activated carbon based samplers.[39] The same research group employed 13X zeolite in combination with activated charcoal strips for testing simultaneously oxygenated solvents and pretroleum-based compounds.[38] Results confirmed initial hypothesis about the preference

of oxygenated solvents to be adsorbed into zeolite whereas charcoal preferably recovered pretroleum products.

4. Extraction of metals

For the determination of metals in different real samples (i.e. environmental, food and biological samples) by atomic emission and absorption spectrometry detection techniques, solid-phase extraction and microextraction techniques are commonly used as sample pretreatment techniques to remove complex matrices, preconcentrate analytes and make the samples suitable for subsequent sample introduction and measurements.[73] Different sorbents such as metal-organic frameworks[74], ion-imprinted polymers[75], magnetic graphene oxides[76], carbon nanotubes[77], among others, have been employed for metal extraction. However, zeolites are considered an attractive alternative to preconcentrate metals from different matrices prior to instrumental analysis, due to their properties described in the Introduction, highlighting its cation-exchange feature. This Section reviews the use of zeolites and zeolite-based materials in (micro)extraction techniques and their different modalities for metals determination. The analytical methods described in this section have been summarized in Table 3.

Table 3. Extraction of metals using zeolites and zeolite-based materials as sorbents.

Sorbent	Analyte	Sample	Extraction technique: conditions	Detection technique	LOD ($\mu g\ L^{-1}$)	Ref.
Natural mordenite	Cu^{2+} Cd^{2+}	Drinking and ground waters	SPE: quartz column packed with 0.6 g of sorbent, 0.5-2 L of sample at pH=6.5 for Cu^{2+} and at pH=5.3 for Cd^{2+}, elution with 10 mL HNO_3/water (1:2 v/v) for Cu^{2+} and with 15 mL NaCl 1 M for Cd^{2+}	FAAS	-[a]	[11]
Natural clinoptilolite	Tb^{3+}	Synthetic waters	SPE: cartridge filled with 0.6 g of sorbent, 0.5-2 L of sample at pH=8.25, elution with 15 mL of 1.0 M NaCl at pH 2.5	UV-vis spectrophotometry	0.75[b]	[26]
Schiff base modified natural analcime	Fe^{3+}	River and drinking waters	SPE: glass column packed with 1 g of analcime, modification with Schiff base in DMF, 50 mL of sample at pH=3.5, elution with 10 mL of 0.1 M EDTA	FAAS	0.084[b]	[14]
L-cystine modified Y zeolite	Cd^{2+}	Water and Plants	SPE: glass column packed with 300 mg of Y zeolite, modification with L-cystine, 100 mL of sample at pH=5.5, elution with 2 mL of 2 M HNO_3	FAAS	0.04[b]	[49]
Zincon-BDTA modified natural analcime	Co^{2+}	Water and biological samples	SPE: funnel tipped glass tube packed with 1 g of analcime, modification with BDTA-Cl and zincon, 30 mL of sample at pH=7, elution with 10 mL of 2 M HCl	FAAS	8[c]	[41]
5-Br-PADAP-BDTA modified natural natrolite	Cu^{2+} Zn^{2+}	Water and biological samples	SPE: funnel tipped glass tube packed with 1 g of BDTA modified natrolite, modification with 5-Br-PADAP, 30 mL of sample at pH=8.5, elution with 5 mL of 2 M HNO_3	FAAS	0.03[b] (Cu^{2+}) 0.006[b] (Zn^{2+})	[52]
Pyrocatechol violet-TDMBA modified natural analcime	Cu^{2+}	Water and biological samples	SPE: funnel tipped glass tube packed with 1 g of TDMBA modified analcime, modification with pyrocatechol violet, 30 mL of sample at pH=7.5, elution with 5 mL of 4 M HNO_3	FAAS	0.05[d]	[42]
Neothorin-BDTA modified Cd-saturated natural clinoptilolite	Zn^{2+}	Well, drinking and waste waters	SPE: glass column packed with 1 g of BDTA modified Cd-saturated clinoptilolite, modification with neothorin, 50 mL of sample at pH=4, elution with 5 mL of 2 M HNO_3	FAAS	0.01[b]	[27]
Neothorin-BDTA modified Zn-saturated natural clinoptilolite	Cd^{2+}	Water and Plants	SPE: glass column packed with 1 g of BDTA modified Zn-saturated clinoptilolite, modification with neothorin, 50 mL of sample at pH=5, elution with 5 mL of 2.5 M HNO_3	FAAS	0.015[c]	[28]
TPPZ-BDTA modified natural analcime	Zn^{2+}	Well, tap and waste waters	SPE: glass column packed with 1 g of sorbent, 50 mL of sample at pH=4, elution with 5 mL of 2 M HNO_3	FAAS	2.9[c]	[43]
BDTA modified Zn-saturated natural analcime	Cd^{2+}	Water and biological samples	SPE: glass column packed with 1 g of sorbent, 10-200 mL of sample at pH=5 with 0.001 M TPPZ, elution with 5 mL of 2 M HNO_3	FAAS	0.02[c]	[44]
BDTA modified Ni-saturated natural clinoptilolite	V^{4+}	Synthetic waters and standard alloys	SPE: funnel tipped glass tube packed with 0.3 g of sorbent, 50 mL of sample at pH=6.5 with 0.001 M PAR, elution with 5 mL of DMF	UV-vis spectrophotometry	0.07[c]	[29]

Sorbent	Analyte	Sample	Method	Detection technique	LOD (μg L⁻¹)	Ref
Zincon-TDMBA modified natural analcime	Pd^{2+}	Spring, river and well waters	SPE: glass column packed with 1 g of analcime, modification with TDMBA -Cl and zincon, 30 mL of sample at pH=3, elution with 5 mL DMSO	TDS	0.25[e]	[45]
Zincon-BDTA modified Cd-saturated natural clinoptilolite	Ni^{2+} Cu^{2+}	Plants	SPE: glass column packed with 1 g of BDTA modified Cd-saturated clinoptilolite, modification with zincon, aliquot of sample at pH=8.5, elution with 5 mL DMF	FDS-HPSAM	0.7[c] (Ni^{2+}) 0.5[c] (Cu^{2+})	[30]
Nitroso-S-BDTA modified Cd-saturated natural clinoptilolite	Cu^{2+} Hg^{2+}	Plant and biological samples	SPE: glass column packed with 1 g of BDTA modified Cd-saturated clinoptilolite, modification with Nitroso-S, 50 mL of sample at pH=8.5, elution with 5 mL DMF	FDS-HPSAM	0.5[c] (Cu^{2+}) 0.1[c] (Hg^{2+})	[31]
Nitroso-S-BDTA modified Cd-saturated natural clinoptilolite	Cd^{2+} Hg^{2+}	Plant and biological samples	SPE: glass column packed with 1 g of BDTA modified Cd-saturated clinoptilolite, modification with Nitroso-S, 50 mL of sample at pH=8.5, elution with 5 mL of DMF	FDS-HPSAM	0.8[c] (Cd^{2+}) 0.1[c] (Hg^{2+})	[32]
5-Br-PADAP-BDTA modified natural analcime	Cd^{2+}	Standard alloys, natural water and biological samples	SPE: funnel tipped glass tube packed with 1 g of BDTA modified analcime, modification with 5-Br-PADAP, 5 mL of sample at pH=9, elution with 5 mL of 2 M HNO_3	ASDPV	0.05[c]	[15]
5-Br-PADAP-BDTA modified natural natrolite and 5-Br-PADAP-BDTA modified natural analcime	Pb^{2+} Cd^{2+}	Aqueous solutions	SPE: funnel tipped glass tube packed with 1 g of BDTA modified natrolite or analcime, modification with 5-Br-PADAP, 0.7-1 L of sample, elution with 5 mL of 2 M HNO_3	ASDPV	-[a]	[46]
PAN-HDTMA modified natural clinoptilolite	Zr^{4+}	Tap and river waters	SPE: funnel tipped glass tube packed with 1 g of HDTMA modified clinoptilolite, modification with PAN, 30 mL of sample at pH=4, elution with 5 mL of 2 M HCl	ICP AES	0.1[b]	[33]
APDC modified NaA zeolite APDC modified NaX zeolite	Cu^{2+}	Tap, ozonized and river waters	SPE: PTFE column packed with 20 mg of NaA or NaX zeolite, on-line modification with APDC, 4 mL of sample at pH=1 for NaA and pH=2 for NaX, on-line elution with 300 μL of MIBK	FI-FAAS	0.1[b] (NaA) 0.4[b] (NaX)	[40]
APDC modified NaY zeolite	Pb^{2+}	Homemade alcoholic drinks	SPE: PTFE column packed with 20 mg of NaY zeolite, on-line modification with APDC, 6 mL of sample at pH=2.5, on-line elution with 100 μL of MIBK	FI-FAAS	1.4-3.5[b]	[50]
APDC modified NaA zeolite APDC modified NaY zeolite APDC modified CaA zeolite APDC modified CaY zeolite	Pb^{2+} Cd^{2+} Ni^{2+} Co^{2+}	Drinking waters	SPE: PTFE column packed with 20 mg of NaA, NaY, CaA or CaY zeolite, on-line modification with APDC, 6 mL of sample, on-line elution with 4 μL min⁻¹ MIBK	FI-FAAS	0.3-1.9[c] (Pb^{2+}) 2.3-5.6[c] (Cd^{2+}) 0.4-0.7[c] (Ni^{2+}) 0.8-2.1[c] (Co^{2+})	[51]
2,6-DAP-PA modified beta zeolite hybrid	Pb^{2+} Ni^{2+} Cu^{2+} Cd^{2+}	Water and Vegetables	SPE: glass column packed with 50 mg of sorbent, 500 mL of water sample and 25 mL of solution of vegetable sample at pH=5.5, elution with 10 mL 1 M HNO_3	FAAS	35[b] (Pb^{2+}) 76[b] (Ni^{2+}) 83[b] (Cu^{2+}) 79[b] (Cd^{2+})	[57]
A-4 zeolite	Cd^{2+}	Lake and river waters and wastewater	D-μ-SPE: 100 mg of sorbent, 100 mL of sample at pH=6, extraction for 20 min, solid phase was separated from the sample by a membrane filter, dissolved with 2 mL of 2 M HNO_3	GFAAS	0.002[b]	[53]

Sorbent	Analyte	Sample	Extraction procedure	Detection	LOD (μg/L)	Ref.
G-CL hybrid	Pb^{2+} Cd^{2+}	Water and human serum	D-μ-SPE: 5 mg of sorbent, 2 mL of water sample or serum sample diluted with deionized water (1:1, v/v) at pH=5, extraction in an ultrasonic bath for 60 s, elution with 100 μL of 0.5 M HNO₃	ETAAS	0.07[b] (Pb^{2+}) 0.004[b] (Cd^{2+})	34
DHPDT modified magnetic NaY zeolite	Cu^{2+} Cd^{2+}	Water and soil	MSPE: 40 mg of sorbent, 10 mL of sample at pH=6, extraction with overhead stirrer for 9 min, upper aqueous phase was used for determination	FI-FAAS	-[a]	19
DDTC-HDTMA modified Zn-saturated ZSM-5/Fe₂O₃	Cd^{2+} Hg^{2+} Pb^{2+}	Urine	MSPE: 50 mg of sorbent, 20 mL of sample at pH=4, manual agitation for 3 min, elution with 432 μL of 11.8 M HNO₃ for 2 min	ICP OES	0.15-0.20[b] (Cd^{2+}) 0.42-0.73[b] (Hg^{2+}) 0.23-0.79[b] (Pb^{2+})	20

LOD, limit of detection; SPE, solid-phase extraction; FAAS, flame atomic absorption spectrometry; UV-vis, ultraviolet-visible; Schiff base, 5-((4-nitrophenylazo)-N-(2´,4´-dimethoxyphenyl))salicylaldimine; DMF, dimethylformamide; EDTA, ethylenediaminetetraacetic acid; zincon, 2-[1-(2-hydroxy-5-sulforphenyl)-3-phenyl-5-formazano]-benzoic acid monosodium salt; BDTA, benzyldimethyltetradecylammonium; BDTA-Cl, benzyldimethyltetradecylammonium chloride; 5-Br-PADAP, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol; TDMBA, tetradecyldimethylbenzylammonium; TDMBA-Cl, tetradecyldimethylbenzylammonium chloride; neothorin, 3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalene disulfonic acid; TPPZ, 2,3,5,6-tetra(2-pyridyl)pyrazine; PAR, 4-(2-pyridylazo)resorcinol; DMSO, dimethylsulfoxide; TDS, third-order derivative spectrophotometry; FDS-HPSAM, first-order derivative spectrophotometry-H-point standard addition method; Nitroso-S, 2-nitroso-1-naphthol-4-sulfonic acid; ASDPV, anodic stripping differential pulse voltammetry; PAN, 1-(2-pyridylazo)-2-naphtol; HDTMA, hexadecyltrimethylammonium; ICP AES, inductively coupled plasma atomic emission spectrometry; APDC, ammonium pyrrolidine dithiocarbamate; PTFE, polytetrafluoroethylene; MIBK, methyl isobutyl ketone; FI-FAAS, flow injection flame atomic absorption spectrometry; 2,6-DAP, 2,6-diacetyl pyridine; PA, 3-aminopropyl trimethoxy silane; D-μ-SPE, dispersive micro-solid-phase extraction; GFAAS, graphite furnace atomic absorption spectrometry; G-CL, graphene-clinoptilolite; ETAAS, electrothermal atomic absorption spectrometry; DHPDT, 2-(3,4-dihydroxyphenyl)-1,3-dithiane; MSPE, magnetic solid-phase extraction; DDTC, sodium diethyldithiocarbamate trihydrate; ICP OES, inductively coupled plasma optical emission spectrometry.

[a] LOD not mentioned by the authors.
[b] Calculated using $3s_{blank}/m$, where s_{blank} is the standard deviation of blank and m is a slope of the calibration curve.
[c] LOD calculation not mentioned.
[d] Calculated using $2s_{blank}/m$, where s_{blank} is the standard deviation of blank and m is a slope of the calibration curve.
[e] Obtained at the optimal instrumental settings (signal-to-noise ratio = 3).

4.1. Solid-phase extraction

A natural mordenite was used by Vasylechko et al.[11] to determine Cu^{2+} and Cd^{2+} in drinking and ground waters by flame atomic absorption spectrometry (FAAS). Firstly, mordenite was thermally treated at 150 °C for 2.5 h to remove the humidity present in the natural zeolites, which affects significantly to their sorption capacity. For SPE, sample solutions adjusted to pH 6.5 and 5.3 for Cu^{2+} and Cd^{2+}, respectively, were passed through a quartz column packed with the mordenite and then, analytes were eluted using HNO_3/water (1:2, v/v) and 1 M NaCl solutions, respectively. The presence of foreign ions in the solution was studied and the results showed a high selectivity of the developed method. Under optimum conditions the extraction efficiency was 99.8% for Cu^{2+} and 94% for Cd^{2+}. Finally, the results obtained with this column were compared with a commercial extraction column "Diapak IDK", obtaining a good agreement. In a later publication, the same research group determined trace amounts of Tb^{3+} in synthetic water samples using a natural clinoptilolite.[26] In this case, clinoptilolite was also heated and stored in a desiccator before using it in SPE. Water samples, adjusted to pH 8.25, were passed through the column containing the zeolite; then Tb^{3+} was eluted from the column with 1 M NaCl solution, and finally determined spectrophotometrically using the method of arsenazo III. Under optimum conditions, an enrichment factor of 130 was obtained. Finally, the method was applied to synthetic water samples obtaining recovery values ranging from 93.3 to 103.0%. Both methods present the advantage that the zeolites were not modified prior to SPE procedure, just thermally activated.

In order to increase the metal preconcentration capacity of zeolites, the modification of the zeolites by different materials (i.e., Schiff base, as 5-((4-nitrophenylazo)-N-(2',4'-dimethoxyphenyl))salicylaldimine, and L-cystine), which act as chelating agents, has been reported. These compounds are immobilized on a zeolite, facilitating the metal retention on the zeolites by complex formation. Related to this, Shamspur et al.[14] developed an analytical method to determine Fe^{3+} in river and drinking water samples by FAAS using a column loaded with natural analcime modified with a new Schiff base, since this ligand forms stable complexes with some transition metals. Firstly, analcime was sieved, washed with 4 M HCl and dried due to its natural origin, therefore, presenting different particle sizes and soluble impurities. This step could be avoided using a synthetic zeolite. Then, the Schiff base was prepared by condensation reaction between a precursor ligand with 2-methoxy-3-nitroaniline in hot ethanol. Some preliminary experiments showed that analcime by itself did not retain Fe^{3+}, while the analcime column modified with a Schiff base showed retention capacity. The authors compared their method with other systems and the main advantages were that natural analcime was low cost, and the LOD value (i.e., 0.084 µg L^{-1}) was much lower than others (i.e, 11[78], 3.3[79] and 12[80] µg L^{-1}). Rezvani et al.[49] proposed Y zeolite modified with L-cystine as new sorbent for the SPE of Cd^{2+} from water and plant samples (i.e., black tea and cigarette's tobacco). Plant samples were previously dried and dissolved in concentrated HNO_3 followed by heating. Then, they were passed through the column packed with L-cystine modified Y zeolite. After extraction, Cd^{2+} sorption was eluted with 2 M HNO_3 for further determination by FAAS. The oxidized form of L-cystine is a good complexing agent due to the presence of two carboxyl

groups, two amino groups and two sulfur atoms in its structure. On the one hand, Fourier Transform Infrared (FT-IR) spectroscopy was applied to demonstrate the adsorption of L-cystine into the zeolite and on the other hand, powder X-ray diffraction (XRD) spectroscopy indicated that L-cystine molecules were physically adsorbed into the zeolite pores without disturbing its original structure. The results of interference study showed that the proposed method was selective for Cd^{2+}, and recoveries and relative standard deviation (RSD) demonstrated the applicability and the excellent repeatability of this method. Finally, L-cystine modified Y zeolite showed equal or better results of LOD, pre-concentration factor, sorbent capacity and repeatability than imprinted polymers, functionalized magnetic nanoparticles and active carbon sorbents.[49]

The modification of the zeolites, firstly, by cationic surfactants (i.e., benzyldimethyltetradecylammonium chloride (BDTA-Cl), tetradecyldimethyl-benzylammonium chloride (TDMBA-Cl) and hexadecyltrimethylammonium bromide (HDTMA-Br)) and then, by different chelating agents has been also reported in different publications.[15,20,27,28,30–33,41–43,45,46,52] In many cases, zeolites cannot adsorb chelating agents molecules because its pore size is smaller than the dimensions of these chelating agents. Additionally, zeolites are negatively charged and, therefore, anionic groups of chelating agents will be repelled from negatively charged zeolite surface. For this reason, to increase the adsorption capacity, the zeolites are first modified with a cationic surfactant.[81] If the surfactant concentration exceeds the critical micelle concentration (CMC), then the hydrophobic tails of the surfactant form a bilayer. Finally, the chelating agent is immobilized on cationic surfactant-coated zeolite since surfactant modified zeolite has positively charged exchange sites formed

43

by the positive groups of the surfactant. An example of the modification of zeolite with surfactant and chelating agent is schematically shown in Fig. 5.
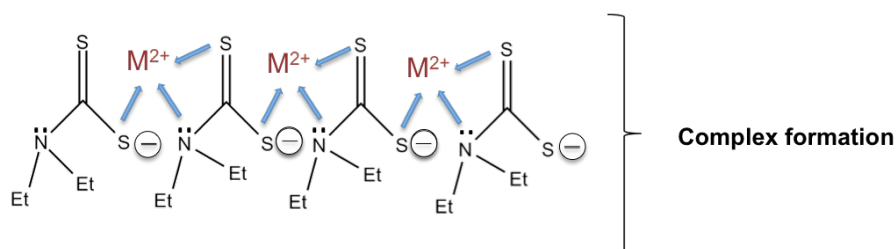
(a)
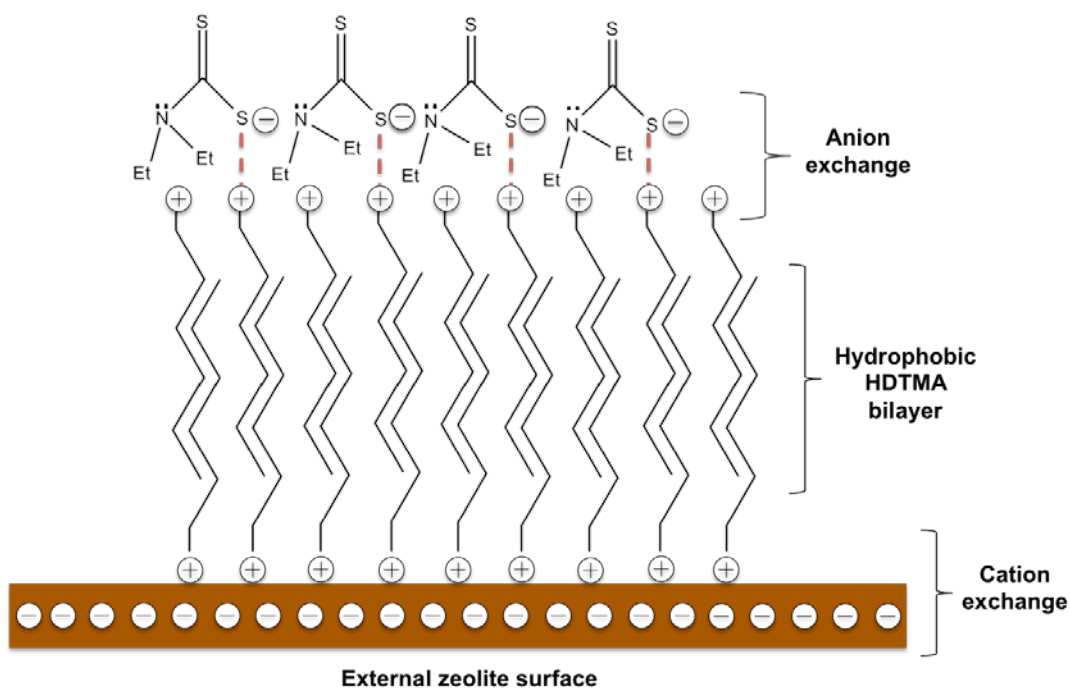
(b)

Fig. 5. Scheme of a zeolite surface modified by HDTMA-Br surfactant and DDTC chelating agent (a) adapted from Ref. [82]; and complex formation of DDTC with M^{2+} cations (b). "Reproduced from Ref. [20] with permission of The Royal Society of Chemistry. Copyright (2018)".

Taher et al. described several analytical methods to determine Co^{2+}[41], Cu^{2+}[42,52], Zn^{2+}[27,52] and Cd^{2+}[28] all in environmental and biological samples using columns loaded with natural zeolites modified with cationic surfactant and chelating agents. In these works, firstly, zeolites were washed with HCl to remove soluble impurities, sieved and washed with HNO_3 to remove the cations, especially Cu or Zn, coming from the natural source of the zeolites. However, these impurities could have affected the Cu or Zn determination even though HNO_3 washes. Secondly, zeolites were modified with BDTA-Cl or TDMBA-Cl. It should be noted that in the first work[41], the surfactant solution was passed through the natural zeolite column, whereas in other works[27,28,42,52], the natural zeolites were previously modified with the surfactant by stirring and then packed in the columns. Finally, different chelating agents, depending on which metal or metals had to be determined (i.e., 2-[1-(2-hydroxy-5-sulforphenyl)-3-phenyl-5-formazano]-benzoic acid monosodium salt (zincon)[41], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP)[52], pyrocatechol violet[42] and 3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalene disulfonic acid (neothorin)[27,28]), were used. In preliminary studies with zeolites and modified zeolites, the authors showed that raw zeolites (i.e., without surfactant and chelating agent) and BDTA or TDMBA modified zeolites (i.e., without chelating agent) were not suitable for the separation and preconcentration of metals because of the low recovery values obtained. However, zeolites modified with BDTA or TDMBA and chelating agents were selective and sensitive for separation and preconcentration of trace amount of the studied metals. In these five studies, the retained metals were desorbed from the column with HNO_3 as eluent, except in the first work[41] in which Co^{2+} was eluted with HCl. In addition,

interference studies showed that among the anions and cations examined, except ethylenediaminetetraacetic acid (EDTA), most of them could be tolerated up to milligram levels. Finally, it should be noted that recoveries and RSD demonstrated the applicability and the excellent repeatability of these five methods.

Following the same research line, Saljooghi et al. proposed a BDTA modified natural analcime for preconcentration of trace amounts of Zn^{2+}[43] and Cd^{2+}[44] from water and biological samples. The main difference with previous methods reported by Taher et al.[27,28,41,42,52] is that the natural analcime, after purification and sieving, was mixed with NH_4NO_3 to exchange Na^+ by NH_4^+, obtaining the NH_4^+-form zeolite and then, it was calcined at 380 ºC to obtain H^+-form to increase its ion-exchange capacity. In the first publication, both BDTA and TPPZ (i.e., 2,3,5,6-tetra(2-pyridyl)pyrazine) modification was carried out in batch mode.[43] However, in the second publication before BDTA modification, the pores of H^+-form of analcime were saturated with Zn to prevent the entrance of analytes into pores of zeolite, so that, adsorption of Cd^{2+} takes place at the outer surface.[44] In addition, the TPPZ chelating agent was added to the sample instead of the sorbent.[44] The influence of analcime particle size in the adsorption of Cd^{2+} was investigated after sieving the analcime to different size ranges (i.e., 0.315–0.180; 0.180–0.140; 0.140–0.125; 0.125–0.11; and <0.110 mm). The accuracy of both methods was evaluated by analyzing reference materials of alloys obtaining recoveries of Zn^{2+} and Cd^{2+} in good agreement with the certified values. Finally, the results obtained with the proposed methods were compared with those obtained by graphite furnace atomic absorption

spectrometry (GFAAS), due to its better sensitivity, demonstrating the applicability of both methods.

All reported publications up to now have employed FAAS as detection technique, except the publication in which Tb^{3+} was determined by UV-vis spectrophotometry.[26] However, other techniques such as UV-vis spectrophotometry[29], derivative spectrophotometry[45], combination of first-order derivative spectrophotometry (FDS) with H-point standard addition method (HPSAM)[30–32], anodic stripping differential pulse voltammetry (ASDPV)[15,46] and inductively coupled plasma atomic emission spectrometry (ICP AES)[33] were employed.

Taher et al. developed several analytical methods using UV-vis spectrophotometers as detection systems, characterized by their simplicity and low cost in comparison with other spectrometric detection systems that require expensive instruments (i.e., ICP AES). A BDTA modified natural clinoptilolite saturated with Ni^{2+} was used as a sorbent for preconcentration and determination of V^{4+} by UV-vis spectrophotometry in synthetic waters and standard alloys.[29] The difference with the previous described methods is that the 4-(2-pyridylazo)resorcinol (PAR) as a chelating agent was added to the sample instead of to the sorbent, except report[44] in which TPPZ was also added to the sample. Then, this solution was passed through the column, containing the BDTA modified Ni-saturated natural clinoptilolite, and the adsorbed complex was eluted with dimethylformamide (DMF). The accuracy of the method was evaluated and the obtained results were in agreement with certified values. Finally, the present method was compared with others methods described in literature and its LOD value (i.e., 0.07 µg L^{-1}) was comparable and lower than

those presented by other methods (i.e., 0.6^{83}, 0.2^{84} µg L^{-1}, among others). The same research group proposed a column packed with TDMBA modified natural analcime loaded with zincon for preconcentration of Pd^{2+} from water samples.[45] The Pd^{2+} complex was eluted from the column with dimethylsulfoxide (DMSO) and determined by third-derivative spectrophotometry. In this work, first TDMBA-Cl solution was passed through the column packed with natural analcime and then, TDMBA modified analcime was modified passing a zincon solution through the column. Both instrumental parameters (i.e, wavelength, scanning speed, wavelength increment over which the derivative is obtained ($\Delta\lambda$) and response time) and reaction conditions (i.e., sample pH, flow rate of the sample and the eluent, nature and volume of eluent) were optimized. Finally, the method was successfully applied to different water samples. Usually, most of the methods that use spectrophotometers suffer from interferences and/or high detection limits. However, by means of derivative spectrophotometry, sharper zero-order bands and a higher signal in the resolution spectra were obtained, solving classical analytical drawbacks of spectrophotometry.

Regarding spectrophotometric techniques, Taher et al. described three analytical methods to determine Ni^{2+}[30], Cu^{2+}[30,31], Hg^{2+}[31,32], and Cd^{2+}[32] from both in plants and biological samples by FDS-HPSAM. HPSAM is one of the mathematical treatment data procedures utilized for the analysis of multicomponent systems. However, in these works HPSAM could not be applied for the simultaneous determination of X and Y metals due to high overlap between their two spectra and the absence of two wavelengths for complexes of X and Y. By FDS, spectra with better resolutions and with two

wavelengths versus the zero-order spectra were obtained. In the three publications, BDTA modified Cd-saturated natural clinoptilolite was packed in a glass column and then, a zincon solution[30] and Nitroso-S (i.e., 2-nitroso-1-naphthol-4-sulfonic acid) solution[31,32] were passed through the column. The adsorbed analytes on the column were eluted with DMF. In the second[31] and third[32] publication, the plant samples, previously digested, were analysed by FAAS and GFAAS, respectively, to compare with the proposed method, obtaining results in good agreement. Finally, it should be noted that in a later publication[32] the column was stable up to at least 30 cycles without decreasing recovery values and the comparison with other methods showed that the time consumption of the proposed method was lower than the others.

Regarding publications in which metals were determined by electroanalytical technique as ASDPV, Afzali et al.[15] developed a procedure using a column of BDTA modified natural analcime and loaded with 5-Br-PADAP for Cd^{2+} preconcentration. The Cd^{2+} retained on the column was eluted with HNO_3, obtaining a preconcentration factor of 140, and finally measured by ASDPV. It should be noted that the RSD was 0.31%, highlighting the excellent repeatability. Finally, this method was successfully applied for the determination of Cd^{2+} in standard alloys, natural water and biological samples. On the other hand, Jamshidi et al.[46], following the same research line, used BDTA modified natural analcime and BDTA modified natural natrolite loaded with the same chelating agent and eluent solvent for Pb^{2+} and Cd^{2+} determination in aqueous samples. The recoveries were higher than 99% for both zeolites and preconcentration factors were 200 and 140 for Pb^{2+} and Cd^{2+}, respectively. The

authors did not provide quality analytical parameters such as linear range, LOD, repeatability, among others, and real samples were not analysed.

Faghihian et al.[33] developed the first method, to our knowledge, to preconcentrate Zr^{4+} in water samples employing a HDTMA modified natural clinoptilolite loaded with 1-(2-pyridylazo)-2-naphthol (PAN) as a chelating agent. Zr^{4+} was eluted with HCl and determined by ICP AES. The applicability of this method was investigated analyzing spiked tap and river water samples, obtaining recoveries higher than 95%. The reuse study confirmed that the column could be used up to 8 times. Compared to previous methods, the LOD of the proposed method was lower than others, and its selectivity versus K^+, Ca^{2+}, Mg^{2+}, NH^{4+}, Na^+, Cl^-, and CH_3COO^- was comparable with other sorbents (i.e., silica gel, vinyl polymer resin, among others). This method employs an ICP AES, which can determine different elements simultaneously, however, just one analyte (i.e., Zr^{4+}) was studied.

All reported publications up to now have employed SPE as extraction technique; however, it presents disadvantages such as the column packing and the time-consuming process of loading large volume of samples. Therefore, some modifications were proposed to the SPE technique as the reduction of sorbent amount.[40,50,51,57] The amount of sorbent to prepare the column was much lower (i.e., 20 or 50 mg) than in the publications mentioned above (i.e., 1 g). The reduction of the amount of sorbent generated advantages such as shorter extraction times and smaller volumes of samples and eluents. Petit de Peña et al.[40] developed a flow injection flame atomic absorption spectrometry (FI-FAAS) for on-line preconcentration and determination of Cu^{2+} using synthetic zeolites. It was the first time that synthetic zeolites were used as

adsorptive material to determine Cu^{2+} traces. In this work, the determination was based on the formation of a chelate of Cu^{2+} with ammonium pyrrolidine dithiocarbamate (APDC). Firstly, columns were packed with 20 mg of NaA and NaX zeolites (i.e., in the report are mentioned as Na-LTA and Na-FAU); secondly, sample and APDC were continuously passed through, then the chelate was eluted with methyl isobutyl ketone (MIBK), and finally Cu^{2+} was determined by FAAS. Comparative studies were carried out using the same amount of C_{18} sorbent. Interferences study showed that synthetic zeolites were more selective than C_{18} sorbent. In addition, comparison of analytical parameters such as LOD, RSD and preconcentration factor showed better results for synthetic zeolites than C_{18}. The zeolite columns were used daily for 2 months with no apparent deterioration in their performance. In a later publication, the same research group used the continuous flow system for the determination of Pb^{2+} in homemade alcoholic drinks.[50] The optimum conditions of adsorption and desorption process were similar to the previous publication. However, in this case only NaY zeolite (i.e., in the report are mentioned as Na-FAU) was used. In this work, due to ethanol and Cu^{2+} strongly interfered in Pb^{2+} determination, ethanol was eliminated by rotaevaporation, and Cu^{2+} was removed by precipitation with rubeanic acid. Finally, it should be noted that preconcentration factors from 80 up to 140 were achieved depending on the sample nature. Nine years later, the same research group[51] determined Pb^{2+}, Cd^{2+}, Ni^{2+} and Co^{2+} in water samples (i.e., drinking waters) following similar procedure than in the two previous publications.[40,50] The synthetic zeolites used to pack the columns (i.e., 20 mg of sorbent) were NaA, NaY, CaA and CaY zeolites (i.e., in the report are mentioned as Na-LTA, Na-FAU, Ca-LTA and Ca-

FAU). CaA and CaY were obtained by ion exchange using a $CaCl_2$ solution starting from NaA and NaY zeolites, respectively. The columns could be used in more than 200 experiments without any loss in its sorption capacity. Under optimum conditions, preconcentration factors from 21 up to 250 were achieved, confirming a high retention of the studied metals.

Finally, it should be mentioned one publication in which Yapati et al.[57] developed a column loaded with 50 mg of a new hybrid sorbent employed to extract Pb^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} from water and vegetable samples. The hybrid sorbent was synthesized by grafting 3-aminopropyl trimethoxy silane (PA) onto beta zeolite (i.e., in the report is mentioned as β-zeolite), and functionalization with 2,6-diacetyl pyridine (2,6-DAP) in a stepwise covalent process. FT-IR spectra of beta zeolite, PA-beta zeolite and 2,6-DAP-PA modified beta zeolite (before and after metal binding) established the successful grafting of the organic moiety on the surface of the beta zeolite and metal chelation with organic functional groups. Additionally, nitrogen adsorption–desorption isotherms of beta zeolite and 2,6-DAP-PA modified beta zeolite showed that the microporous structure was not disturbed even after surface modification. However, the surface area, pore size and pore volume of beta zeolite decreased after surface modification. The accuracy of the method was estimated by analyzing reference standard materials, obtaining under optimum conditions a good trueness and RSD was lower than 3.1%. It should be mentioned that LODs values of this method (i.e., 35, 76, 83 and 59 µg L^{-1} for Pb^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+}, respectively) are slightly higher than those review in the literature for the same purpose (Table 3).

4.2. Dispersive micro-solid-phase extraction

Unlike high number of reported SPE publications using zeolites as sorbents for metal extraction, only two publications have been reported for D-μ-SPE technique.[69,71] On one hand, Minamisawa et al.[53] developed a method for the preconcentration and determination of Cd^{2+} in water samples using A-4 zeolite and GFAAS detection technique, respectively. Even though the authors considered the procedure as SPE, the work has been included in this section because the sorbent was not packed in a column but directly dispersed in the sample. In preliminary experiments several types of inorganic adsorbents (i.e., A-4 zeolite, F-9 zeolite, X-13 zeolite and alumina) were investigated, obtaining better recoveries with A-4 zeolite. Extraction procedure consisted on dispersing 100 mg of A-4 zeolite into the sample by conventional stirring, then separation of the sorbent from the sample by a membrane filter, and finally, it was dissolved in 2 M HNO_3. It is important to point out that the feature of this method was the direct injection of the sample solution (i.e., this solution containing Cd^{2+} and the dissolved A-4 zeolite) into the graphite furnace. According to this, the solubility of A-4 zeolite and the viscosity of the resulting solution were investigated using HCl and HNO_3. The results showed that HNO_3 was more effective for the dissolution of A-4 zeolite. However, the dissolution of the zeolite could be a disadvantage because there is no reuse possibility. The authors highlighted that the method was simple, fast and a high preconcentration factor (i.e., 400) was obtained. On the other hand, Ghazaghi et al.[34] described a hybrid nanoadsorbent prepared by depositing graphene over the natural clinoptilolite (G-CL) by chemical vapor deposition to preconcentrate Pb^{2+} and Cd^{2+} from water and human serum by ultrasound

assisted D-μ-SPE. The nanoadsorbent was characterized by field emission scanning electron microscopy (FE-SEM) (Fig. 6), XRD, and energy dispersive X-ray (EDX) microanalysis, all of which revealed the high surface area of the graphene sheets on the natural clinoptilolite.
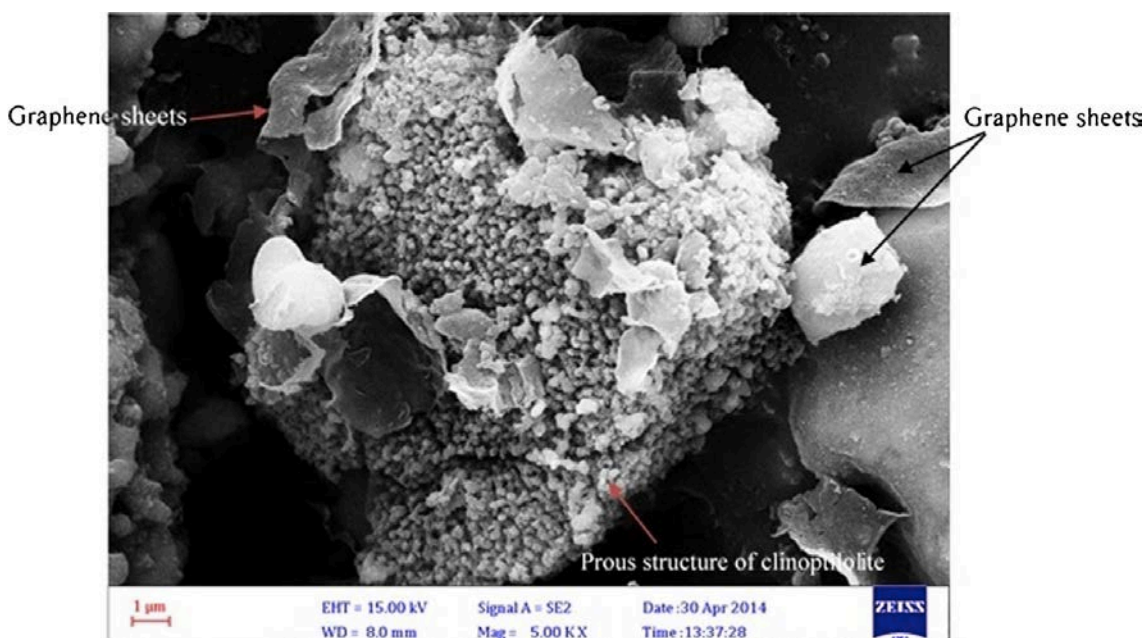

Fig. 6. FE-SEM image of G-CL hybrid. "Reprinted from Ref. [23] with permission. Copyright (2015) Springer".

Comparison between G-CL hybrid and natural clinoptilolite as sorbents showed that efficiency of natural clinoptilolite both in water and serum samples was lower than that obtained with the G-CL hybrid, highlighting the low recoveries obtained for serum with natural clinoptilolite (i.e., lower than 9%) versus recoveries higher than 97% using G-CL hybrid. This could be related with the fact that metal ions are bonded to proteins and large biomolecules, therefore graphene sheets were a barrier against the macromolecules, so metal ions can penetrated through the porous structure of clinoptilolite, while part of the metal ions that bonds with the proteins of plasma, can be adsorbed on the

surface of the graphene, so whole the metal ions (free and bonded) can be extracted. The main advantages of this method were that both sample volume (i.e., 2 mL) and sorbent amount (i.e., 5 mg) were very low, and therefore, suitable for biological approaches. Additionally, metal ions could be adsorbed without any chelating agent.

4.3. Magnetic solid-phase extraction

To our knowledge, only two publications have reported up to now about the use of zeolites decorated with magnetic nanoparticles as sorbent for preconcentration of heavy metals. In the first publication, 2-(3,4-dihydroxyphenyl)-1,3-dithiane (DHPDT) modified magnetic NaY zeolite was presented as a new sorbent for MSPE. In this work, Shirani et al.[19] determined Cd^{2+} and Cu^{2+} in water and soil samples by FAAS. Firstly, magnetic NaY zeolite was synthesized mixing NaY zeolite in NH_4OH solution with $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 4H_2O$ in HCl solution under a nitrogen atmosphere by ultrasonic treatment. Then, DHPDT modified magnetic NaY zeolite was prepared by magnetic stirring NaY zeolite with DHPDT in a methanol solution. The magnetic curve in Fig. 7 shows the appropriate superparamagnetic property of the magnetic modified NaY zeolite as seen by the lack of a hysteresis loop and no remanence existence. It should be noted that in the extraction procedure the sorbent was separated and the upper aqueous phase (i.e., supernatant) containing the residual Cd^{2+} and Cu^{2+} in the solution was used for determination by FI-FAAS. A three-layer artificial neural network model was developed to predict the simultaneous removal of Cd^{2+} and Cu^{2+}. The results indicated that

the proposed artificial neural network model could perfectly predict the process showing a close correlation between the experimental and predicted values.
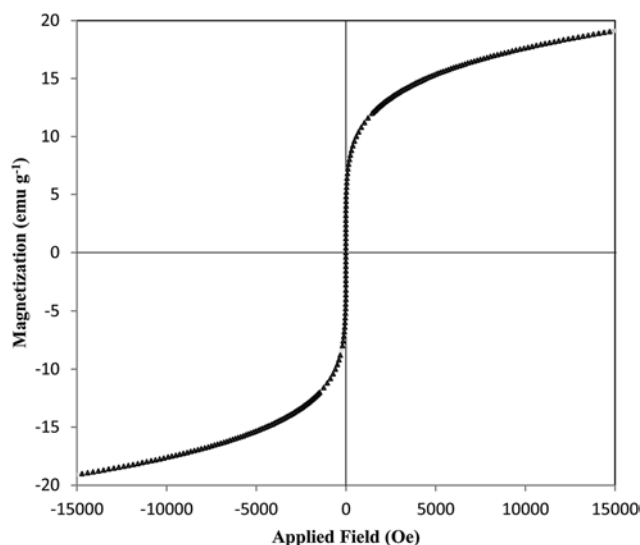

Fig. 7. The hysteresis loop of the magnetic organo-modified zeolite. "Reproduced from Ref.[16] with permission of The Royal Society of Chemistry. Copyright (2015)".

The sorbent was reused up to 3 times showing constant adsorption efficiency, but it needed a previous regeneration. Finally, the comparison of the evaluation parameters of the proposed method with other methods such as adsorption time, sorbent mass and sorption capacity showed better results. Considering these results, authors concluded that the novel DHPDT modified magnetic NaY zeolite could be properly applied in an industrial scale. Finally, it should be mentioned a recent report published by our research group to determine Cd^{2+}, Hg^{2+} and Pb^{2+} in urine samples by inductively coupled plasma optical emission spectrometry (ICP OES).[20] This work employed a composite based on ZSM-5 zeolite decorated with magnetic iron oxide nanoparticles (i.e., ZSM-5/Fe_2O_3). This composite was first impregnated with Zn and then modified

with HDTMA-Br and sodium diethyldithiocarbamate trihydrate (DDTC) (i.e., DDTC-HDTMA-Zn-ZSM-5/Fe_2O_3). Comparison between ZSM-5/Fe_2O_3, Zn-ZSM-5/Fe_2O_3 and DDTC-HDTMA-Zn-ZSM-5/Fe_2O_3 showed that efficiency of DDTC-HDTMA-Zn-ZSM-5/Fe_2O_3 in urine samples was higher than the obtained with the other sorbents. A possible explanation was that urine contains certain compounds (i.e., proteins and large biomolecules) that act as chelating agents and could, therefore, form complexes with the studied analytes (i.e., Hg). A two-step multivariate strategy, using Plackett-Burman and circumscribed central composite designs, was employed to optimize experimental parameters affecting MSPE. Finally, good extraction efficiencies were obtained for Hg^{2+} and Pb^{2+} and the low value obtained for Cd^{2+} could be explained through the compromised extraction conditions chosen. However, the LOD values satisfy the threshold limit established by the Ministry of Labour and Social Affairs (Spain) for normal content of these metals in human urine and by the World Health Organization for normal mercury content in urine.[85,86]

5. Conclusions

Natural and synthetic raw zeolites have been successfully employed for the extraction of organic compounds and metals. However, most of the studies done up to date employ zeolites modified with different reagents such as surfactants, chelating agents and metallic particles, among others. These modifications offer a wide range of extraction possibilities because the desired properties can be easily tuned. Another important aspect to point out is the versatility of the zeolites to distinct conformations upon request, mainly as a thin-film, packed in a cartridge, disperse in solutions and as a SPME fiber. Additionally, the whole procedure (i.e., synthesis, modification, extraction system assembly, etc.) can be lab made, what goes in the direction to open source philosophy. Despite these advantages, zeolites also possess some limitations. For instance, the widespread use of modified zeolites evidences the boundary of raw zeolites, especially for organic compounds extraction. Furthermore, most of the studies are devoted to the determination of a single analyte, being less environmental friendly methodologies; and only four studies have developed automated procedures,[13,40,50,51] what could be fixed as a goal in the near future.

On the other hand, zeolites have strong competitors in the extraction field such as other ordered mesoporous materials, molecularly imprinted polymers or metal-organic frameworks. However, zeolites present some advantages over other materials. For example, their natural origin or economical synthesis procedure (in case of synthetic zeolites) provides zeolites in large amounts being considered low cost sorbents. The high chemical and water stability makes zeolites robust materials, being able to work not only under mild

conditions but also in heavy environments. Based on this statement, zeolite and zeolite-based materials can be reused for numerous extractions without significant alterations in their performance, doing the procedure more environmentally friendly.

To conclude, Granda Valdés et al.[3] already highlighted the great analytical potential of these materials, but their potential is still waiting to be exploited 12 years later. Additionally, every year new zeolites are being discovered or synthesized, thus opening the gate towards the exploration and discovery of new challenges.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

References

1   B. Trewyn, *Heterogeneous catalysis for today's challenges: synthesis, characterization and applications*, Royal Society of Chemistry Publishing, Cambridge, 2015.

2   S. M. Auerbach, K. A. Carrado and P. K. Dutta, *Handbook of zeolite science and technology*, Marcel Dekker, New York, 2003.

3   M. G. Valdés, A. I. Pérez-Cordoves and M. E. Díaz-García, *TrAC Trends Anal. Chem.*, 2006, **25**, 24-30.

4   S. Wang and Y. Peng, *Chem. Eng. J.*, 2010, **16**, 11-24.

5   Structure Commission of the International Zeolite Association, *http://www.iza-structure.org/*, (July 2018).

6   C. Martínez and J. Pérez-Pariente, *Zeolites and ordered porous solids: fundamentals and applications*, Universitat Politècnica de València, Valencia, 2011.

7   O. Marincas, P. Petrov, T. Ternes, V. Avram and Z. Moldovan, *J. Phys. Conf. Ser.*, 2009, **182**, 012040.

8   E. Fernández and L. Vidal, in *Miniaturization in Sample Preparation*, ed. F. Pena-Pereira, De Gruyter OPEN, Warsaw, 2014, pp. 191-237.

9   C. F. Poole, *TrAC Trends Anal. Chem.*, 2003, **22**, 362-373.

10 C. L. Arthur and J. Pawliszyn, *Anal. Chem.*, 1990, **62**, 2145-2148.

11 V. O. Vasylechko, L. O. Lebedynets, G. V. Gryshchouk, R. Leboda and J. Skubiszewka-Zieba, *Chem. Anal.*, 1999, **44**, 1013-1024.

12 P. Arnnok and R. Burakham, *J. Braz. Chem. Soc.*, 2014, **25**, 1720-1729.

13 P. Arnnok, N. Patdhanagul and R. Burakham, *Chromatographia*, 2015, **78**, 1327-1337.

14 T. Shamspur, I. Sheikhshoaie and M. H. Mashhadizadeh, *J. Anal. At. Spectrom.*, 2005, **20**, 476-478.

15 D. Afzali, A. Mostafavi, M. A. Taher, E. Rezaeipour and M. Khayatzadeh Mahani, *Anal. Sci.*, 2005, **21**, 383-386.

16 A. Mollahosseini, M. Toghroli and M. Kamankesh, *J. Sep. Sci.*, 2015, **38**, 3750-3757.

17 S. Zhou, Z. Li, X. Lv, B. Hu and Q. Jia, *Analyst*, 2015, **140**, 5944-5952.

18 E. Fernández, L. Vidal and A. Canals, *J. Chromatogr. A*, 2016, **1458**, 18-24.

19 M. Shirani, A. Akbari and M. Hassani, *Anal. Methods*, 2015, **7**, 6012-6020.

20 P. Baile, L. Vidal, M. Á. Aguirre and A. Canals, *J. Anal. At. Spectrom.*, 2018, **33**, 856-866.

21 Y. S. Al-Degs, A. H. El-Sheikh, M. A. Al-Ghouti, B. Hemmateenejad and G. M. Walker, *Talanta*, 2008, **75**, 904-915.

22 Y. S. Al-Degs and J. A. Sweileh, *Arab. J. Chem.*, 2012, **5**, 219-224.

23 D. Bergé-Lefranc, H. Pizzala, R. Denoyel, V. Hornebecq, J. L. Bergé-Lefranc, R. Guieu, P. Brunet, H. Ghobarkar and O. Schäf, *Micropor. Mesopor. Mater.*, 2009, **119**, 186-192.

24 T. Pasinli and E. Henden, *Ekoloji*, 2013, **22**, 57-66.

25 X. Chen, S. Chen, J. Liu and J. Wang, *Microchim. Acta*, 2009, **165**, 217-222.

26 V. O. Vasylechko, G. V. Gryshchouk, V. P. Zakordonskiy, O. Vyviurska and A. V. Pashuk, *Chem. Cent. J.*, 2015, **9**, 45-51.

27 S. Hajialigol, M. A. Taher and A. Malekpour, *J. AOAC Int.*, 2008, **91**, 1446-1452.

28 A. Malekpour, S. Hajialigol and M. A. Taher, *J. Hazard. Mater.*, 2009, **172**, 229-233.

29 L. Rostampour and M. A. Taher, *Talanta*, 2008, **75**, 1279-1283.

30 R. Roohparvar, M. A. Taher and A. Mohadesi, *J. AOAC Int.*, 2008, **91**, 637-645.

31 A. Mohadesi, R. Roohparvar and M. A. Taher, *Trans. Univ. Kosice*, 2008, **3**, 112-119.

32 S. Z. Mohammadi, R. Roohparvar and M. A. Taher, *J. Anal. Chem.*, 2016, **71**, 42-49.

33 H. Faghihian and M. Kabiri-Tadi, *Microchim. Acta*, 2010, **168**, 147-152.

34 M. Ghazaghi, H. Shirkhanloo, H. Z. Mousavi and A. M. Rashidi, *Microchim. Acta*, 2015, **182**, 1263-1272.

35 M. C. Dumlao, L. E. Jeffress, J. J. Gooding and W. A. Donald, *Analyst*, 2016, **141**, 3714-3721.

36 S. Goda, R. Selyanchyn, T. Nozoe, H. Matsui and S. W. Lee, *J. Anal. Bioanal. Tech.*, 2014, 004/1-004/7.

37 T. P. Lee, B. Saad, E. P. Ng and B. Salleh, *J. Chromatogr. A*, 2012, **1237**, 46-54.

38 C. L. Rodgers, K. A. St. Pierre and A. B. Hall, *Forensic Sci. Int.*, 2014, **240**, 144-150.

39 K. A. St. Pierre, V. J. Desiderio and A. B. Hall, *Forensic Sci. Int.*, 2014, **240**, 137-143.

40   Y. Petit De Peña, W. López, J. L. Burguera, M. Burguera, M. Gallignani, R. Brunetto, P. Carrero, C. Rondon and F. Imbert, *Anal. Chim. Acta*, 2000, **403**, 249-258.

41   M. A. Taher, A. Mostafavi and S. Z. Mohammadi, *Asian J. Chem.*, 2005, **17**, 1456-1462.

42   D. Afzali, A. Mostafavi, M. A. Taher and A. Moradian, *Talanta*, 2007, **71**, 971-975.

43   A. S. Saljooghi, S. J. Fatemi and D. Afzali, *Bull. Chem. Soc. Ethiop.*, 2010, **24**, 127-132.

44   A. S. Saljooghi and Z. S. Saljoghi, *Toxicol. Ind. Health*, 2012, **28**, 771-778.

45   M. A. Taher, A. Mostafavi and S. Z. Mohammadi, *J. Anal. Chem.*, 2007, **62**, 1022-1027.

46   R. Jamshidi, Z. Afzali and K. Afzali, *Asian J. Chem.*, 2009, **21**, 3381-3384.

47   P. Arnnok, N. Patdhanagul and R. Burakham, *Talanta*, 2017, **164**, 651-661.

48   P. Salisaeng, P. Arnnok, N. Patdhanagul and R. Burakham, *J. Agric. Food Chem.*, 2016, **64**, 2145-2152.

49   S. A. Rezvani and A. Soleymanpour, *J. Chromatogr. A*, 2016, **1436**, 34-41.

50   Y. Petit De Peña, B. Paredes, W. Rondón, M. Burguera, J. L. Burguera, C. Rondón, P. Carrero and T. Capote, *Talanta*, 2004, **64**, 1351-1358.

51   Y. Petit De Peña and W. Rondón, *Am. J. Anal. Chem.*, 2013, **4**, 387-397.

52   A. Mostafavi, D. Afzali and M. A. Taher, *Anal. Sci.*, 2006, **22**, 849-853.

53   H. Minamisawa, R. Okunugi, M. Minamisawa, S. Tanaka, K. Saitoh, N. Arai and M. Shibukawa, *Anal. Sci.*, 2006, **22**, 709-713.

54   Y. Tao, Y. Jiang, W. Li and B. Cai, *RSC Adv.*, 2016, **6**, 98476-98486.

55   W. B. Wilson, A. A. Costa, H. Wang, J. A. Dias, S. C. L. Dias and A. D. Campiglia, *Anal. Chim. Acta*, 2012, **733**, 103-109.

56   W. B. Wilson, A. A. Costa, H. Wang, A. D. Campiglia, J. A. Dias and S. C. L. Dias, *Microchem. J.*, 2013, **110**, 246-255.

57   H. Yapati, S. Bhogineni, S. Chirumamilla and K. Seshaiah, *J. Chem. Sci.*, 2016, **128**, 779-786.

58   F. Augusto, L. W. Hantao, N. G. S. Mogollón and S. C. G. N. Braga, *TrAC Trends Anal. Chem.*, 2013, **43**, 14-23.

59   A. Mehdinia and M. O. Aziz-Zanjani, *TrAC Trends Anal. Chem.*, 2013, **51**, 13-22.

60   J. Xu, J. Zheng, J. Tian, F. Zhu, F. Zeng, C. Su and G. Ouyang, *TrAC Trends Anal. Chem.*, 2013, **47**, 68-83.

61   N. Gilart, F. Borrull, N. Fontanals and R. M. Marcé, *Trends Environ. Anal. Chem.*, 2014, **1**, e8-e18.

62   B. H. Fumes, M. R. Silva, F. N. Andrade, C. E. D. Nazario and F. M. Lanças, *TrAC Trends Anal. Chem.*, 2015, **71**, 9-25.

63   A. A. Matin, R. Maleki, M. A. Farajzadeh, K. Farhadi, R. Hosseinzadeh and A. Jouyban, *Chromatographia*, 2007, **66**, 383-387.

64   A. Chalabiani, A. A. Matin and K. Farhadi, *J. Chinese Chem. Soc.*, 2012, **59**, 1080-1085.

65   H. Wang, Z. Li, Q. Niu, J. Ma and Q. Jia, *Appl. Surf. Sci.*, 2015, **353**, 1326-1333.

66 D. Bergé-Lefranc, O. Schäf, R. Denoyel, J. L. Bergé-Lefranc, R. Guieu, P. Brunet and V. Hornebecq, *Micropor. Mesopor. Mater.*, 2010, **129**, 144-148.

67 Z. Du, J. Mo, Y. Zhang, X. Li and Q. Xu, *Anal. Methods*, 2013, **5**, 3463-3472.

68 M. Ghazi-Khansari, R. Zendehdel, M. Pirali-Hamedani and M. Amini, *Clin. Chim. Acta*, 2006, **364**, 235-238.

69 M. Cruz-Vera, R. Lucena, S. Cárdenas and M. Valcárcel, *Anal. Methods*, 2011, **3**, 1719-1728.

70 S. Risticevic, V. H. Niri, D. Vuckovic and J. Pawliszyn, *Anal. Bioanal. Chem.*, 2009, **393**, 781-795.

71 J. Płotka-Wasylka, N. Szczepańska, M. de la Guardia and J. Namieśnik, *TrAC Trends Anal. Chem.*, 2015, **73**, 19-38.

72 A. A. Costa, W. B. Wilson, H. Wang, A. D. Campiglia, J. A. Dias and S. C. L. Dias, *Micropor. Mesopor. Mater.*, 2012, **149**, 186-192.

73 M. He, L. Huang, B. Zhao, B. Chen and B. Hu, *Anal. Chim. Acta*, 2017, **973**, 1-24.

74 Ş. Tokalıoğlu, E. Yavuz, S. Demir and Ş. Patat, *Food Chem.*, 2017, **237**, 707-715.

75 F. Shakerian, K. H. Kim, E. Kwon, J. E. Szulejko, P. Kumar, S. Dadfarnia and A. M. Haji Shabani, *TrAC Trends Anal. Chem.*, 2016, **83**, 55-69.

76 J. Sun, Q. Liang, Q. Han, X. Zhang and M. Ding, *Talanta*, 2015, **132**, 557-563.

77   A. I. Corps Ricardo, A. Sánchez-Cachero, M. Jiménez-Moreno, F. J. Guzmán Bernardo, R. C. Rodríguez Martín-Doimeadios and Á. Ríos, *Talanta*, 2018, **179**, 442-447.

78   S. Saraçŏlu and L. Elçi, *Anal. Chim. Acta*, 2002, **452**, 77-83.

79   V. Gurnani, A. K. Singh and B. Venkataramani, *Anal. Chim. Acta*, 2003, **485**, 221-232.

80   N. Pourreza and H. Z. Mousavi, *Talanta*, 2004, **64**, 264-267.

81   B. Armağan, M. Turan and M. S. Çelik, *Desalination*, 2004, **170**, 33-39.

82   M. Anari-Anaraki and A. Nezamzadeh-Ejhieh, *J. Colloid Interface Sci.*, 2015, **440**, 272-281.

83   S. Boudra, J. M. Bosque-Sendra and M. C. Valencia, *Talanta*, 1995, **42**, 1525-1532.

84   J. Wang, D. Lu, S. Thongngamdee, Y. Lin and O. A. Sadik, *Talanta*, 2006, **69**, 914-917.

85   World Health Organization, *Guidelines for drinking-water quality*, Geneva, 2008.

86   INSHT, *NTP 109: Biological threshold values for metals exposures monitoring*, Ministry of Labour and Social Affairs (Spain), 1984.