Microchim Acta (2013) 180:703–710
DOI 10.1007/s00604-013-0971-1

SHORT COMMUNICATION

Rapid extraction and determination of atrazine and its degradation products from microporous mineral sorbents using microwave-assisted solvent extraction followed by ultra-HPLC-MS/MS

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Received: 30 January 2013 / Accepted: 26 February 2013 / Published online: 15 March 2013

Abstract We have evaluated three methods for the extraction of atrazine and six of its degradation products from microporous mineral sorbents. Soxhlet extraction and ultrasonic extraction, which work well on soils and sediments, recover only <15 % of the atrazine from a dealuminated Y zeolite. Closed-vessel microwave-assisted extraction, in contrast, gives much better recoveries. This is attributed to the accelerated mass transfer at elevated temperatures and the displacement by the solvent forced into the mineral micropores under elevated pressures. Under the optimized conditions, the recovery of atrazine from the hydrophilic Y zeolites (Si/Al ratios <8) is almost quantitative, and ~77 % for the more hydrophobic ones. The extraction efficiencies for the degradation products of atrazine in the hydrophilic zeolites (74.1–100 %) are also higher than those in the hydrophobic ones (22.3–44.2 %). The extracted compounds were quantified by a combination of ultra-HPLC and tandem MS and resulted in detection limits between 0.04 and 1.41 mg kg^{-1} on a hydrophilic Y zeolite (Si/Al=2.55), and of 0.09–2.35 mg kg^{-1} on a hydrophobic zeolite (Si/Al=15). The method was applied to study the degradation of atrazine sorbed on dealuminated Y zeolites.

Keywords Atrazine · Degradation products · Microporous mineral · Hindered molecular diffusion · Microwave-assisted extraction · Ultra-HPLC/MS/MS

Introduction

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-S-triazine], which is one of the most widely used herbicides, has been applied in agriculture and forestry for several decades [1, 2]. Due to its low sorption on soils and sediments and slow degradation, atrazine is frequently detected in surface and ground waters, often at concentrations up to the μg L^{-1} level [3–5]. Atrazine is a known endocrine-disrupter, and is suspected to be carcinogenic even at very low concentrations [1, 2, 4]. Atrazine can be degraded to a range of less toxic degradation products, including hydroxyatrazine, deethylatrazine, deisopropylatrazine, N-isopropylammeline, N-ethylammeline, and ammeline by microorganisms in nature and biological treatment process, and by ozone and OH radicals in ozonation and advanced oxidation processes [6–8].

As a result of its widespread use, atrazine has become the most common herbicide contaminant of ground and surface waters [9–11]. Adsorption by activated carbon, an efficient and effective method for removal of organic contaminants, has been commonly used for removing atrazine in potable water treatment [12]. Our research has shown that microporous minerals can serve as excellent sorbents for organic contaminants and minerals with more hydrophobic pore spaces exhibit higher sorption capacities [13–15]. Dealuminated Y zeolites with high Si/Al ratios have been observed to exhibit high sorption capacities towards atrazine [16, 17]. Consequently, microporous minerals are good candidates for sorbents used in packed

Electronic supplementary material The online version of this article (doi:10.1007/s00604-013-0971-1) contains supplementary material, which is available to authorized users.

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columns, similar to activated carbon, for removing atrazine from aqueous stream. They can also be applied as "reactive" materials for removing atrazine from contaminated groundwater in permeable reactive barrier, which is an innovative and cost-effective in situ groundwater remediation technology [18].

The effectiveness of microporous minerals for atrazine removal depends on their sorption capacities and the mass of atrazine sorbed on them, which requires periodic monitoring of the masses of atrazine (and its degradation products) sorbed. Organic contaminants are sorbed predominantly within the hydrophobic micropores of these mineral sorbents, instead of on the external surfaces as in the cases of soils and sediments. Despite the availability of a range of extraction approaches, selection of an appropriate method for quantitative recovery of atrazine from microporous minerals can be difficult. Because the desorption rate from micropores is very slow due to hindered molecular diffusion in the molecular dimension pore spaces [13–15, 19, 20], conventional extraction techniques that work well on soils and sediments, such as Soxhlet extraction and ultrasonic extraction [21, 22], may no longer be effective.

As far as we know, no previous study has investigated the extraction of organic contaminants from microporous mineral sorbents. The objective of this study was to develop a method for rapid recovery and determination of atrazine and its degradation products in microporous mineral sorbents. The efficiencies of Soxhlet extraction, ultrasonic extraction, and microwave-assisted extraction (MAE) were compared, and only MAE was found to be able to achieve high recoveries of atrazine from the microporous mineral sorbents. The conditions of MAE (solvent composition, and extraction temperature and time) were further optimized to improve the extraction efficiency. Ultra-HPLC and tandem MS analytical procedure was also developed for selective and accurate determination of atrazine and its degradation products in the extracts. The method was validated and applied to study degradation of atrazine sorbed in dealuminated Y zeolites.

Experimental

Chemicals and reagents

Analytical grade atrazine (98.4 %), hydroxyatrazine (99.0 %), deethylatrazine (98.0 %), N-ethylammeline (99.5 %), and ammeline (98.0 %) were purchased from Dr. Ehrenstorfer (Augsburg, Germany, www.ehrenstorfer.com). Deisopropylatrazine (98.0 %) and N-isopropylammeline (95.0 %) were supplied by AccuStandard (New Haven, Connecticut, USA, www.accustandard.com). HPLC grade methanol, acetone, and dichloromethane were obtained from CNW Technologies (Dusseldorf, Germany, www.cnwtech.eu). Triple distilled water made in-house from an all glass distillation apparatus was used in the preparation of all aqueous solutions.

A series of dealuminated Y zeolites obtained from Zeolyst (Valley Forge, PA, USA, www.zeolyst.com) were evaluated as model microporous mineral sorbents (Table S1, Electronic Supplementary Material (ESM)). They have identical microporous framework structure but different levels of surface hydrophobicity due to dealumination. A grounded silica sand with median diameter of 8 μm obtained from U.S. Silica (Berkeley Springs, WV, USA, www.ussilica.com), was also selected as a reference for nonporous mineral sorbent (Table S1, ESM). The zeolites were calcined at 380 °C for 12 h and the silica sand was heated at 200 °C for 5 h prior to use.

Extractions

Soxhlet extraction of the mineral sorbents (~0.2 g) was carried out using 150 mL of dichloromethane at 40 °C for 72 h. Compared to dichloromethane, methanol and acetone have higher boiling points and lower vapor pressures, and are flammable, while atrazine has good solubility in all of them (Table S2, ESM). As a result, only dichloromethane was evaluated as the extraction solvent in Soxhlet extraction. Ultrasonic extraction of the mineral sorbents (~0.2 g) was conducted by equilibrating with 20 mL of dichloromethane at 25 °C for 12 h, followed by sonication at 30 °C for 30 min. Each sample was extracted three times with fresh solvent. More details are summarized in the ESM.

MAE was conducted with a MARS microwave extraction system with programmable power and irradiation time by CEM (Matthews, NC, USA, www.cem.com), equipped with 14 pressurized 100 mL Greenchem TFA-lined extraction vessels. The unit generates a multimode microwave at 2.45 GHz, and its magnetron produces continuous unpulsed microwave output ranging from 0 to 1,600 W. During the course of extraction, a rotating magnetic plate positioned below the microwave cavity rotated the Teflon-coated stir bars in each vessel to improve solid/solution contact. MAE was performed in closed-vessel mode, with the temperature in the extraction vessels controlled by the variable microwave power output that was adjusted continuously based on the feedback from a fiber-optic temperature sensor inserted in the control vessel. The extraction vessels can withstand a maximum pressure of 200 psig, and the in-vessel pressure during extraction was indirectly controlled by the extraction temperature. The mineral sorbents (~0.2 g) were extracted with 20 mL of extraction solvent. The composition of extraction solvent, and extraction time and temperature were varied to optimize the extraction conditions. The vessels were opened after fully cooling down, and the supernatants

(2–3 mL) were withdrawn by glass syringes and filtered with 0.22 μm PTFE membrane filters.

Ultra-HPLC/MS/MS analysis

The identification and quantification of atrazine and its degradation products in the extracts were accomplished on an ultra-high performance liquid chromatograph-triple quadrupole tandem mass spectrometer (TSQ Vantage, Thermo Scientific, USA, www.thermoscientific.com) equipped with electrospray ionization (ESI). The chromatographic column was an Acquity BEH C18 analytical column (50 mm×2.1 mm) with 1.7 μm particle size (Waters, Milford, MA, USA, www.waters.com), and the injection volume was 5 μL. The analytes were eluted within 4.0 min by methanol-water (70:30, *v*/*v*) containing 0.2 % formic acid. The mobile phase flow-rate was 0.2 mL min^{-1} and the column temperature was maintained at 40 °C. The ionization and fragmentation settings of the mass spectrometer were optimized by direct injection of the respective standard solution of each analyte at 5 μL min^{-1}. The following working conditions were applied to the mass spectrometer: spray voltage at 4 kV; vaporizer and capillary temperatures at 350 and 290 °C, respectively; sheath and auxiliary gas at 30 and 5 arbitrary units (a.u.), respectively; cycle time of 1 s. Argon pressure in the collision cell (Q2) was set at 1.5 mTorr and the mass resolution at the first (Q1) and third (Q3) quadrupoles was set at 0.7 Da full width at half maximum (FWHM). Precursor ion, S-lens RF amplitude, and collision energy in Q2 were optimized individually per compound or transition. Quantification and confirmation data were acquired in selected reaction monitoring (SRM) mode following the transitions shown in Table 1. Instrument control and data processing were carried out by the Xcalibur 2.2 SP1 software. Analyte quantification was performed by comparison with the calibration curves established with mixed standard solutions. Blanks and standards were also run regularly.

Recovery study

As no standard reference material was available, spiked mineral sorbents were used to evaluate the extraction efficiencies by different methods. Spiked samples were prepared by adding 100 μL of solution of atrazine and its degradation products (4 mgL^{-1} each) to 0.2 g of mineral sorbents. The slurries were then equilibrated at room temperature for 1 day. Although water content of the solid sample can affect the efficiency of MAE [23], our tests (by adding 50–300 μL of atrazine solution) showed that the extraction efficiency was not significantly influenced by the mineral sorbent's water content (data not shown). The exact masses of atrazine and its degradation products loaded on the spiked samples (0.2 g each) were accurately known by preparing them individually, instead of spiking the sorbents in bulk. The recovery efficiencies were calculated as the ratios between the masses recovered in the extracts and those spiked on the mineral sorbents.

Results and Discussion

Comparison of extraction methods

Soxhlet extraction is efficient and is generally regarded as a benchmark technique for the extractions of semi-volatile organic compounds from solid matrix [24]. Figure 1a compares the performance of Soxhlet extraction, ultrasonic extraction, and MAE at recovering atrazine sorbed on the silica sand and CBV-720. For the silica sand, Soxhlet extraction and ultrasonic extraction (both using dichloromethane) achieved reasonably good recovery efficiencies (55–65 %). For the microporous CBV-720, only 6.6 % of the sorbed atrazine could be removed by Soxhlet extraction, while 14.3 % of the sorbed atrazine mass was recovered by the ultrasonic extraction repeated three times. Compared to the nonporous

Table 1 MS/MS parameters of the MRM acquisition mode for analysis of atrazine and its degradation products

Analyte	CAS No.	Precursor ion ($[M+H]^+$) (*m/z*)	Product ions (*m/z*)	S-lens (RF amplitude) (V)	Collision energy (eV)
Atrazine	1912-24-9	216	174[a]/146	75	6[b]/12
Hydroxyatrazine	2163-68-0	198	156[a]/128	68	14[b]/27
Deethylatrazine	6190-65-4	188	146[a]/104	66	17[b]/23
Deisopropylatrazine	1007-28-9	174	132[a]/104	63	16[b]/22
N-isopropylammeline	–	170	128[a]/85	72	10[b]/20
N-ethylammeline	–	156	128[a]/85	66	14[b]/22
Ammeline	645-92-1	128	85[a,c]	66	20[b]

[a] Product ion of the quantitative transition (the unmarked one represents that of the confirmation transition)

[b] Collision energy of the quantitative transition (the unmarked one represents that of the confirmation transition)

[c] Confirmation transition was not used due to limitation of instrument sensitivity

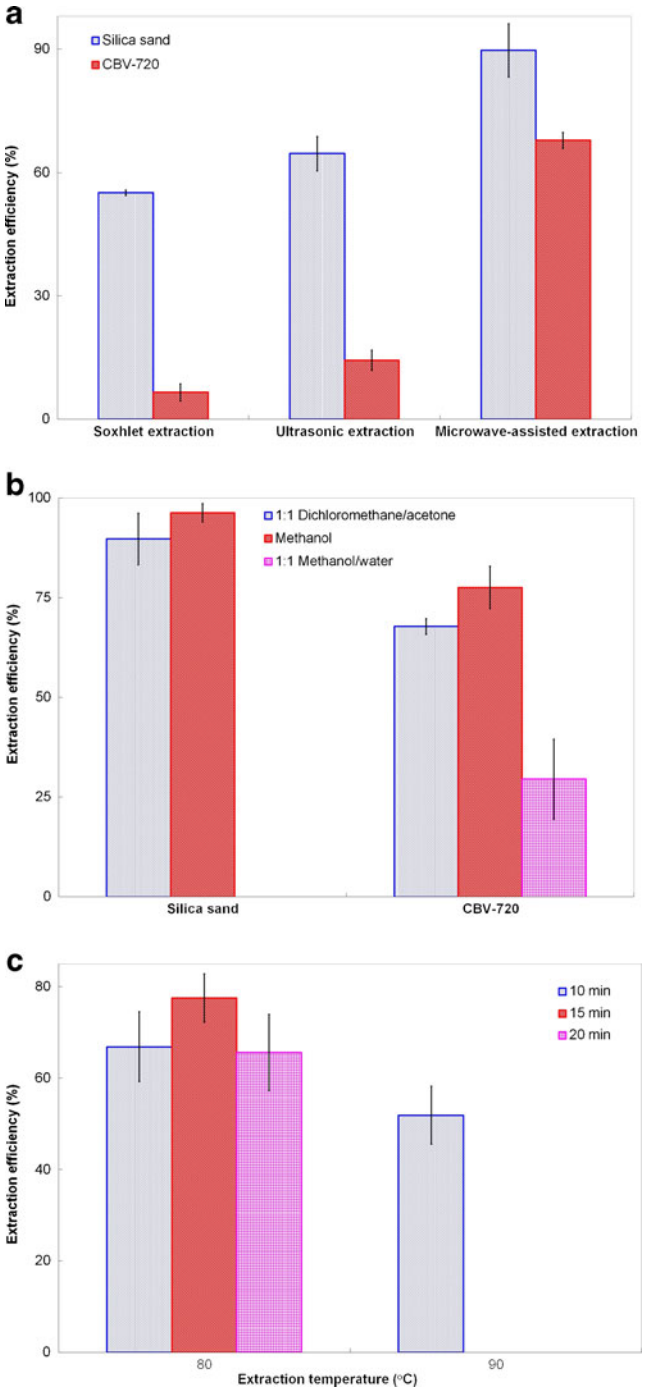

Fig. 1 Comparison of the efficiencies of three extraction methods and optimization of MAE conditions: **a** performance of Soxhlet extraction, ultrasonic extraction, and MAE at recovering atrazine from the essentially nonporous silica sand and the microporous CBV-720; **b** optimization of extraction solvent composition for recovering atrazine from the silica sand and CBV-720 by MAE (conducted at 80 °C for 15 min); and **c** optimization of extraction temperature and time for recovering atrazine from CBV-720 by MAE (with 20 mL of methanol). *Error bars* represent standard deviation from the mean (n=3)

silica sand, extraction of atrazine from CBV-720 was much more difficult, which could be attributed to the sorption of atrazine molecules in the hydrophobic micropores of the zeolite [16, 17]. With the small pore diameters (0.74–1.2 nm), desorption of atrazine from the zeolite micropores is rather slow due to hindered molecular diffusion [13–15, 19, 20]. Despite the rather long sample-solvent contacting times in both Soxhlet extraction and ultrasonic extraction, these techniques could not efficiently extract atrazine from microporous minerals.

As microwave heating results from the direct effect of microwaves on molecules by ionic conduction and dipole rotation [25], a polar solvent with high dielectric loss, acetone, was added to dichloromethane at *v*/*v* ratio of 1:1 to form a solvent mixture. MAE conducted with 20 mL of 1:1 dichloromethane/acetone removed 89.7 and 67.8 % of the sorbed atrazine from the silica sand and CBV-720 after 15 min of extraction at 80 °C (Fig. 1a). The mass transfer rates of the analytes from the sample matrix are significantly accelerated in MAE with the microwave heating of the solvent in contacting with the solid sample [23]. The pressures within the closed extraction vessels were also high with the solvent staying at a temperature (80 °C) above its boiling point (Table S2, ESM). Consequently, the solvent molecules could be forced into the micropores of the mineral sorbents, causing displacement of the sorbed atrazine molecules. Both effects contributed to the drastically improved recovery of atrazine from the microporous CBV-720 by MAE compared to Soxhlet extraction and ultrasonic extraction.

Optimization of MAE conditions

The conditions of MAE were further optimized to improve the atrazine extraction efficiency. The most commonly studied parameters in the optimization of MAE conditions include solvent composition, solvent volume, extraction temperature, and extraction time [23]. Figure 1b compares the performance of 1:1 dichloromethane/acetone, methanol, and 1:1 methanol/water as the extraction solvents in MAE. The results show that methanol/water mixture performed poorly. As atrazine is only moderately soluble in water (33 mgL^{-1} at 25 °C), the methanol/water mixture is expected to have a relatively low solubility towards atrazine. Furthermore, the extraction was carried out at a temperature (80 °C) that was just above the boiling point of the 1:1 methanol/water mixture (Table S2, ESM). As a result, the pressures within the closed extraction vessels were not much higher above atmospheric pressure, which could be partially responsible for the observed low extraction efficiency. In contrast, MAE with methanol yielded better results than 1:1 dichloromethane/acetone under comparable extraction conditions. Atrazine is soluble in methanol (15 gL^{-1} at 25 °C) and the extraction temperature is well above its boiling point (Table S2, ESM). The high atrazine recovery achieved by

methanol was probably due to the fact that it could better penetrate into the micropores of CBV-720 and cause displacement of the sorbed atrazine more efficiently with its smaller molecular size compared to those of dichloromethane and acetone. The amount of solvent recommended for the 100 mL Greenchem extraction vessel is between 10 and 30 mL. As the finely powdered mineral sorbents (~0.2 g) could be well dispersed in the solvent under constant stirring, the solvent volume (20 mL) was sufficient for the extraction and thus not optimized in this study.

Temperature is an important factor affecting the efficiency for essentially all extraction techniques because elevated temperatures facilitate desorption of analytes from the active sites of the solid matrix, the "hotter" solvent has a higher capacity to solubilize analytes, and the sample wetting and matrix penetration are also improved with reduced surface tension and viscosity of the solvent at higher temperatures [23]. Figure 1c shows the influence of extraction temperature and time on atrazine recovery from CBV-720. Significant reduction in the extraction efficiency occurred when the temperature was increased from 80 to 90 °C with an extraction time of only 10 min. This is attributed to the degradation of atrazine, which is thermolabile, at elevated temperatures. MAE is highly efficient and extraction times of no more than 15 min are often sufficient for extraction of organic pollutants [21, 26, 27]. At 80 °C, increasing the extraction time from 10 to 15 min led to appreciable improvement in the extraction efficiency, while reduction in the atrazine recovery occurred (due to thermal degradation) with further increase of the extraction time to 20 min (Fig. 1c). Based on the above observations, the optimal MAE conditions were: 20 mL of methanol at 80 °C for 15 min under continuous microwave irradiation. No indication of atrazine degradation was observed under such conditions, and 96.3 and 77.1 % of the atrazine sorbed on the silica sand and CBV-720 could be extracted, respectively. No significant difference in the recovery was observed for the same sorbent spiked with different concentrations of atrazine. Compared to Soxhlet extraction and ultrasonic extraction, the MAE method developed here is not only highly efficient and rapid, but also significantly reduces the toxicity of the extraction solvent and the solvent volume.

Method validation

Figure 2a shows the atrazine extraction efficiencies on four dealuminated Y zeolites (CBV-100, CBV-712, CBV-720,

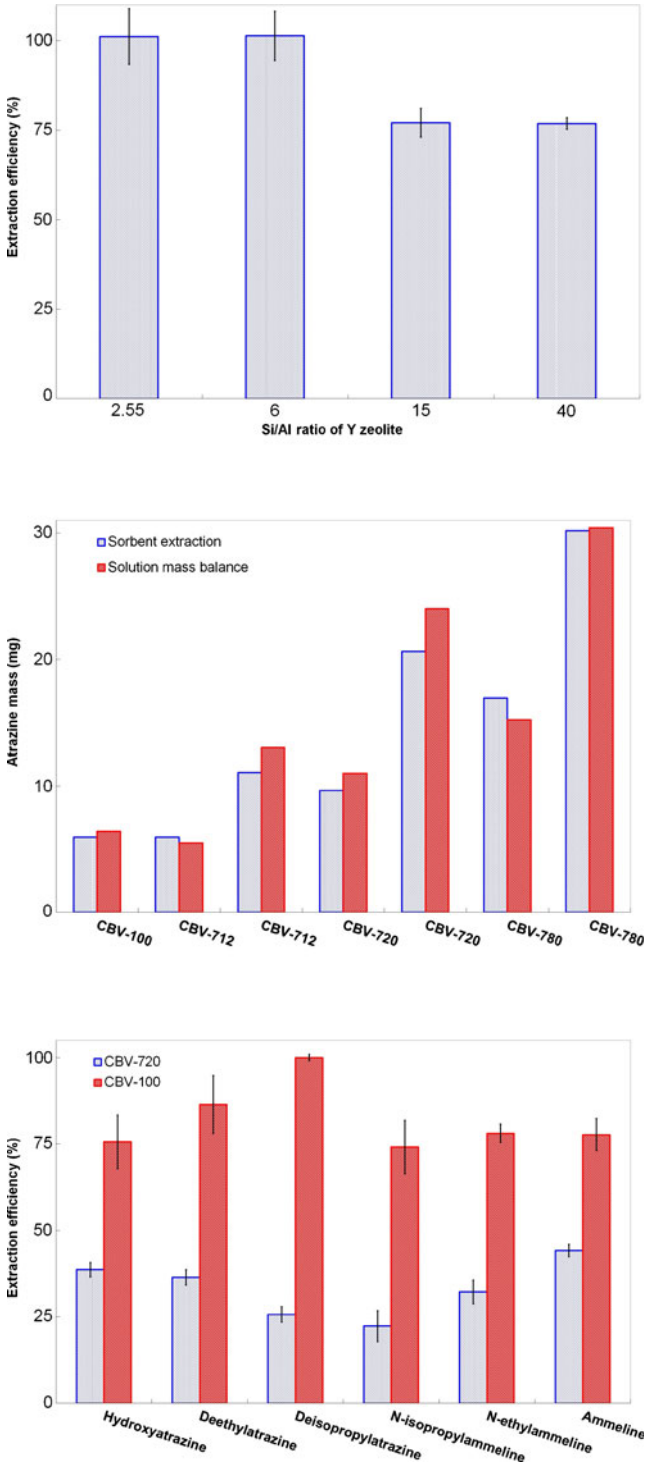

Fig. 2 Validation of the MAE method at atrazine recovery and its performance at recovering the degradation products of atrazine: **a** atrazine extraction efficiencies from a series of dealuminated Y zeolites with increasing Si/Al ratios; **b** comparison of atrazine contents in 4 dealuminated Y zeolites that had been equilibrated with atrazine solutions quantified from MAE followed by ultra-HPLC/MS/MS detection with those calculated from mass balance of the aqueous solutions. CBV-100 was equilibrated with a solution containing 3.56 mg L^{-1} atrazine, while the other zeolites were equilibrated with 0.89 and 1.78 mg L^{-1} atrazine solutions. The mass balance results of the atrazine sorbed on the zeolites were obtained by multiplying the concentration differences of the aqueous solutions with the solution volume (20 mL); and **c** recovery of the six degradation products of atrazine from the micropores of CBV-720 and CBV-100 under the conditions optimized for atrazine extraction. *Error bars* represent standard deviation from the mean (n=3)

and CBV-780) achieved by MAE under the optimized conditions. For the Y zeolites with low Si/Al ratios of 2.55 (CBV-100) and 6 (CBV-712), near quantitative recovery of atrazine could be achieved, while the extraction efficiencies were approximately 77 % for those with much higher Si/Al ratios (CBV-720 and CBV-780). Zeolites with higher Si/Al ratios are more hydrophobic, and the transition from hydrophilic to hydrophobic typically occurs at the Si/Al ratio of 8 [20, 28]. Atrazine molecules sorbed predominantly in the hydrophobic micropore spaces of the Y zeolites, and possibly formed hydrogen bonding with the water molecules in the hydrophilic pore spaces through the lone pair of electrons on N atoms [29, 30]. The extraction efficiency results indicate that removal of atrazine sorbed in the micropores of the hydrophobic zeolites is much more difficult compared to that sorbed in the hydrophilic ones.

The MAE method was validated by comparing the atrazine contents of zeolites that had been equilibrated with atrazine solutions quantified from MAE and ultra-HPLC/MS/MS detection with those calculated from mass balance. About 0.2 g of zeolites were equilibrated with 20 mL of atrazine solution for 24 h. The atrazine contents of the zeolites were determined based on the masses recovered by MAE and the extraction efficiencies. Alternatively, the masses of atrazine sorbed on the zeolites were also calculated from mass balances of the aqueous solutions. Figure 2b compares the results obtained with both approaches, and shows that MAE followed by ultra-HPLC/MS/MS detection could quantify the masses of atrazine sorbed on these microporous mineral sorbents with good accuracy.

Recovery of atrazine degradation products by MAE

As the primary compound of interest in this study is atrazine, the conditions optimized for atrazine extraction were also used for the degradation products. Figure 2c summarizes the recovery efficiencies of the atrazine degradation products from CBV-720 and CBV-100 by MAE. The extraction rates of the atrazine degradation products in CBV-100 (74.1–100 %) were much higher than those in CBV-720 (22.3–44.2 %), probably because these compounds sorbed more strongly in the more hydrophobic micropores. The recovery efficiencies for the atrazine degradation products on both zeolites were lower compared to those of atrazine, which could be explained by the stronger sorption of these more polar compounds (compared to atrazine) in the mineral micropores.

Linear dynamic ranges, linearity, and detection and quantification limits

The calibration graphs for ultra-HPLC/MS/MS analysis of atrazine and its degradation products were obtained by using

Table 2 Limits of detection (LODs), limits of quantification (LOQs), regression coefficients (r), and linear dynamic ranges for analysis of atrazine and its degradation products in microporous mineral sorbents

Analyte	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	r	Linear dynamic ranges (mg L^{-1})
Atrazine				
CBV-100	0.07	0.22	0.9995	0.001-1
CBV-720	0.09	0.29		
Hydroxyatrazine				
CBV-100	0.17	0.56	0.9990	0.005-0.1[a]
CBV-720	0.31	1.01		
Deethylatrazine				
CBV-100	0.09	0.30	0.9985	0.005-0.1[a]
CBV-720	0.19	0.66		
Deisopropylatrazine				
CBV-100	0.04	0.13	0.9980	0.005-0.1[a]
CBV-720	0.16	0.51		
N-isopropylammeline				
CBV-100	0.26	0.84	0.9970	0.005-0.1[a]
CBV-720	0.81	2.65		
N-ethylammeline				
CBV-100	0.24	0.78	0.9935	0.005-0.1[a]
CBV-720	0.56	1.83		
Ammeline				
CBV-100	1.41	4.68	0.9995	0.005-0.1[a]
CBV-720	2.35	12.01		

[a]Concentration above 0.1 mg L^{-1} was not measured because of the compound's poor solubility in methanol

Table 3 Masses of atrazine and its degradation products recovered from CBV-720 and CBV-100 after microwave irradiation treatment using the developed method

Compound mass (nmol)[a]	CBV-720, after microwave irradiation for						CBV-100, after microwave irradiation for					
	0 min	2 min	4 min	6 min	8 min	10 min	0 min	2 min	4 min	6 min	8 min	10 min
Atrazine	750.2	726.8	702.1	639.2	585.9	349.9	289.0	281.4	273.4	265.7	231.9	201.8
Hydroxyatrazine		1.8	3.1	12.2	23.1	53.4		1.8	1.7	3.7	8.3	19.1
Deethylatrazine		4.6	4.7	5.6	8.5	6.0		1.3	16.8	11.1	8.8	7.5
Deisopropylatrazine		7.0	7.8	7.2	5.6	4.4		1.3	5.3	4.7	3.7	3.1
N-isopropyl-ammeline		0.9	1.0	1.1	1.3	1.2		0.3	0.9	0.4	0.2	0.3
N-ethyl-ammeline		5.8	6.6	6.0	6.3	6.7		2.4	3.8	3.2	2.6	2.7
Ammeline				3.4	4.8	4.5			2.0	3.2	2.5	2.2
Sum of all compounds	750.2	747.1	725.3	674.6	635.4	426.1	289.0	288.6	303.9	291.9	258.0	236.6

[a] The quantities of atrazine and its degradation products are expressed on molar basis instead of mass basis to indicate the changes of these species during the degradation process

standard solutions of the seven analytes in methanol. The linear dynamic ranges for atrazine and its degradation products are summarized in Table 2. Good linearity was observed and the regression coefficients were between 0.9935 for N-ethylammeline and 0.9995 for atrazine and ammeline. The precision of the mass spectrometric determination was estimated by analyzing a standard solution of atrazine and its degradation products at 0.1 mgL^{-1} five times on ultra-HPLC/MS/MS. The repeatability of the mass spectrometric determination, expressed as the relative standard deviation (RSD), was no greater than 2.8 % for all the analytes.

Application of the method to the analysis of atrazine and its degradation products

The method was applied to study the degradation of atrazine sorbed on CBV-720 and CBV-100 after microwave irradiation (ESM). In the absence of abundant solvent in the surrounding environment, microwave irradiation caused formation of micro-scale "hot spots" in the mineral micropores and degradation of the sorbed atrazine via pyrolysis [16, 17]. Table 3 shows the masses of atrazine and its degradation products recovered from CBV-720 and CBV-100 as a function of microwave irradiation time. Hydroxyatrazine, deethylatrazine, deisopropylatrazine, N-isopropylammeline, N-ethylammeline, and ammeline were formed from atrazine degradation, and they degraded further with continuous microwave irradiation. Conservation of the atrazine mass was not observed because only six degradation products were monitored here and some of the degradation products were probably mineralized to small molecules such as CO_2 and H_2O. The results demonstrate that the developed method can be used for determining the masses of atrazine and its degradation products in microporous mineral sorbents.

Conclusions

Quantitative recovery of organic compounds sorbed on microporous minerals is challenging because of the slow release rates from micropores. Although Soxhlet extraction and ultrasonic extraction could often obtain satisfactory results for recovering organic contaminants from soils and sediments, they essentially failed at recovering the atrazine sorbed on the microporous mineral sorbent in this study. A method based on closed-vessel MAE followed by ultra-HPLC/MS/MS detection was developed for rapid determination of atrazine and its degradation products in microporous mineral sorbents. The optimal extraction conditions were: 20 mL of methanol, continuous microwave irradiation for 15 min to maintain a steady extraction temperature of 80 °C. Ultra-HPLC/MS/MS could selectively and accurately quantify the concentrations of atrazine and its degradation products in the obtained extracts. The developed method shows good performance in terms of analyte recoveries, analytical precision, linearity, and limits of detection and quantification. Compared to Soxhlet extraction and ultrasonic extraction, closed-vessel MAE carried out at temperatures above the boiling points of the extraction solvents greatly accelerates the desorption rates of analytes from the mineral micropores. Furthermore, it requires much less solvent, and significantly reduces the extraction time while allowing a high sample throughput (i.e., multiple samples can be extracted simultaneously). Experimental results demonstrate that the method developed here is reliable and efficient, and is well suited for rapid determination of atrazine and its degradation products in microporous mineral sorbents.

Acknowledgement The authors are grateful to the reviewers' valuable comments that improved the manuscript. This work was supported in parts by the Natural Science Foundation of China (Grant Nos. 41073079 and 41121063) and the Chinese Academy of Sciences (Y234081001 and "Interdisciplinary Collaboration Team" program). This is contribution No. IS-1639 from GIGCAS.

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