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Application of activated carbon in the characterization of nitrogen compounds and phthalates in a landfill leachate

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Abstract

The goal of this work was the development of a methodology based on solid phase extraction (SPE) to characterize nitrogen compounds and phthalates from landfill leachate samples. Activated carbon (AC) was used to extract all the organic compounds from the samples. The samples were collected in Porto Alegre–South Brazil. As the AC used had small particle size, it was impossible to use it in the form of packed cartridges; hence, it had to be applied in a batch mode. The desorption of the organic compounds from the AC was made by sonication with dichloromethane. The extract was analyzed by gas chromatography with mass spectrometric detection (GC–MSD). Some aspects of the validation of the methodology were also established. Several nitrogen compounds and phthalates were identified in the samples, proving the efficiency of this method with regard to the selectiveness for these substances.
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1. Introduction

Solid phase extraction (SPE) is a powerful technique for the extraction of organic compounds from aqueous samples [1,2]. The procedure is based on the adsorption of the material at the surface of a solid [2] and can be applied to extract organic compounds from aqueous samples by using various sorbents such as Amberlyst XAD resins [3–6], C-18 silica cartridges [7] and others.

The performance of SPE is critically dependent on the sorption capacity of the solid phase and the contact time between the solute and the sorbent. SPE is normally performed using columns or cartridges, but when the sorbent has a small particle size, this form is not adequate because the procedure is not only time consuming, it also includes the risk of losses. In this particular case, it is preferable to use the batch technique.

Activated carbon (AC) is one of the most used sorbents and has a wide variety of applications in several processes of the chemical industry, such as water and wastewater treatment. AC is especially effective in removing soluble organic compounds from surface water and groundwater sources [8–10], and it can be used for the extraction of neutral, nonpolar and polar organic compounds from aqueous samples [7]. Its sorption capacity is so strong that, in many cases, the adsorption process is irreversible.

Knowing the high sorption capacity of AC, the main purpose of this work was to adapt it to the SPE procedure without the use of cartridges or columns, due to the small particle size of AC. For the desorption step, an ultrasonic extraction was investigated.

It is well known that the use of sonication facilitates the desorption of organic compounds from the active carbon. This technique has numerous advantages, such as: (a) high reproducibility, (b) applicability to a large range of sample sizes, (c) reduction in time to perform efficient extraction when compared with another methods and (d) efficient desorption of polar organic compounds, which were strongly adsorbed at the surface of the AC [3,4].

The methodology was developed with some standards and applied to a sample of landfill leachate from Porto Alegre, RS, Brazil.

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2. Experimental

2.1. Equipment

A gas chromatograph with mass spectrometric detector (Shimadzu QP5050A) was used in the electronic impact ionization mode at 70 eV and with an HP-5 (Polymethylsiloxane with 5% of phenyl groups) fused silica open tubular column, with 60 m length×0.30 mm i.d.×0.25 μm film thickness. The temperature program was started at 50 °C for 10 min, heated at 2 °C min^{-1} to 300 °C, and left at this temperature for 10 min. The split/splitless injector, in the split mode (1:50), was kept at 280 °C and the interface was kept at 300 °C. Helium was used as carrier gas at a flow rate of 1.0 ml min^{-1}. For quantitative purposes, the gas chromatography with mass spectrometric detection (GC–MSD) was used in the Single Ion Monitoring (SIM) mode and the monitored ions were 77, 91, 141 and 149.

A sonication bath model Thorton T-14, potency of 90 W, 40 kHz of frequency and 0.27 W cm^{-2} of radiation intensity was used. The dimensions of the bath were 24×14×10 cm.

2.2. Reagents

All solvents (Merck) were of analytical reagent grade (p.a.), and bidistilled. Powdered AC (Merck) was purified by Soxhlet extraction with dichloromethane for 24 h and dried in an oven at 105 °C overnight. The following chromatographic standard compounds were purchased from Sigma Aldrich: ethyl toluene sulfonamide (ETS), butyl benzene sulfonamide (BBS), diisobutyl phthalate (DIBP), dibutyl phthalate (DBP) and dioctyl phthalate (DOP).

Individual stock solutions of each of the standard compounds (3000 mg l^{-1}) were prepared using dichloromethane as the solvent. From these stock solutions, another standard solution was prepared with all the compounds at 1000 mg l^{-1}. Finally, the spike aqueous solutions, required to carry out the experiments, were prepared by dilutions of this standard solution.

2.3. Samples

The sample of landfill leachate was collected from a sanitary landfill located in Porto Alegre, Rio Grande do Sul, Brazil. This landfill receives municipal solid wastes exclusively. Samples were collected in dark glass flasks and maintained under refrigeration for no more than 2 weeks.

The samples were previously filtered and characterized by pH, biochemical oxygen demand after 5 days (BOD$_5$) and chemical oxygen demand (COD) measurements, by the monitoring system of the Municipal Department of Urban Cleaning (DMLU).

3. Procedure

3.1. Adsorption

In an Erlenmeyer flask, 5 g of NaCl was added to 100 ml of the sample (or the spike solution), in order to reduce the attraction between water and organic compounds, then 1.0 g of the AC was added. In order to promote the adsorption of the organic compounds to the AC, the sample was stirred for 45 min using a magnetic stirring bar coated with Teflon and left in rest for 10 min. After this, the mixture was centrifuged for 10 min to separate the phases. The water phase was discharged and the solid phase (AC with the adsorbed organic material—AC/OM) was dried at 110 °C for 10 min to remove the excess of water.

3.2. Desorption

Dichloromethane (30 ml) was added to the AC/OM, and the mixture was submitted to ultrasonic extraction for 15 min and filtered afterwards. The process was repeated three times and the solid portion was discharged after that, while the organic solutions were combined and the volume reduced to 1 ml. The sample was analyzed and the organic compounds were characterized by GC–MSD.

The efficiency of the method was determined by the recovery, which is calculated by using spike solutions at 100 mg l^{-1} and samples fortified with these standards also at 100 mg l^{-1}. Other parameters, such as limit of detection (LOD), limit of quantification (LOQ), linearity and repeatability were also determined.

Water from a MILLI-Q system (Millipore, Bedford, MA) was used to determine the method blank, after it had been submitted to the same methodology (AC adsorption, centrifugation and dichloromethane extraction by sonication). This analysis was always accomplished in parallel with the analysis of the samples or of the spike solutions.

4. Results and discussion

The initial characterization of the landfill leachate samples, collected between January 2002 and May 2003, presented pH values around 8.0, and high indexes of organic matter, estimated by the variation of COD (values between 1700 and 4200 mg O$_2$ l^{-1}) and BOD$_5$ (between 400 and 2000 mg O$_2$ l^{-1}).

Blank analysis demonstrated that no contaminants were present in the system, including solvents, sorbents and glassware.

Table 1 shows the figures of merit for the five compounds using the proposed methodology. Although multiple steps are involved upon the analysis, the values calculated for the percentage recovery using spiked solutions prior to analysis were satisfactory for the routine purposes. The study of the linearity was performed by using standard

Table 1
Figures of merit for the developed methodology

Compounds	Rec. (%)	r^2	LOD (mg l^{-1})	LOQ (mg l^{-1})	RSD (%)
ETS	99.3	1.0000	0.12	0.38	4.7
BBS	87.3	0.9999	0.075	0.25	9.3
DIBP	76.7	0.9951	0.053	0.18	0.82
DBP	64.5	0.9989	0.030	0.098	7.0
DOP	101	0.9847	0.062	0.20	8.3

rec. (%): recovery; r^2: correlation coefficient; LOD: limit of detection; LOQ: limit of quantification; RSD: relative standard deviation.

solutions at five concentration levels, from 100 to 500 mg l^{-1} of the target analyte, and the correlation coefficients found show a good linear relationship. The detection limit, LOD, the lowest analyte concentration that produces a response detectable above the noise level of the system, typically, three times the noise level and the quantification limit, LOQ, the lowest level of analyte that can be accurately and precisely measured, were also in an acceptable range for the analysis of landfill leachates, which are complex environmental samples. This LOQ is required only for impurity methods and was calculated as the analyte concentration that gives S/N=10. S/N represents the signal/noise ratio in the chromatogram. The method precision obtained in the analysis of the five standard compounds positively identified is reflected in the relative standard deviation; based on peak area, sample and injection repeatability (*n*=3), this demonstrates that the proposed methodology has good repeatability.

Fig. 1 shows the chromatogram of the extract obtained from the analyzed landfill sample, and Table 2 shows the peak identification of this figure. In this table, only the five standard compounds used in the optimization of the method were positively identified. The others were only tentatively identified, i.e., only with the help of the library of the GC–

Table 2
Identification of the marked peaks in Fig. 1

Peak	Formula	Name	Identification*
1	C_6H_6	benzene	MS
2	C_5H_5N	pyridine	MS
3	C_7H_8	cycleheptatriene	MS
4	C_3H_7NO	*n,n*-dimethyl formamide	MS
5	$C_6H_{18}O_3Si_3$	hexamethyl cyclehexasiloxane	MS
6	$C_5H_4O_2$	furfural	MS
7	C_7H_6O	benzaldehyde	MS
8	$C_8H_{24}O_4Si_4$	octamethylcycletetrasiloxane	MS
9	$C_7H_{14}O$	epoxi-dimethylpentane	MS
10	$C_9H_{12}O$	phenyl-propanol	MS
11	$C_5H_{12}N_2O$	*n*-dimethyl-*n*-nitroso-propanamine	MS
12	$C_5H_6N_2O_3$	dimethyl-trioxoimidazolidine	MS
13	$C_7H_9NO_2$	ethyl-methyl-pirrolidone	MS
14	$C_6H_9N_3O_2$	*n,n*-trimethyl-dioxotriazine	MS
15	$C_8H_{10}N_2S$	*n*-methyl-*n*-phenyl-tiourea	MS
16	$C_{12}H_{18}O_4$	cyclepropanodicarboxilic acid, isopropenyl diethyl ester	MS
17	$C_{10}H_{12}O_3$	hidroxi-metoxi-dimethylbenzaldehyde	MS
18	$C_{11}H_{14}O_2$	hydroxi-methylethyl-phenyl ethanone	MS
19	$C_{11}H_{14}NO_2$	dimethylamine toluyl azapropenone	MS
20	$C_9H_{13}NO_2S$	*N*-ethyl toluene sulfonamide	MS, ST
21	$C_9H_{13}NO_2S$	*N*-ethyl-*N*-methyl benzenosulfonamide	MS
22	$C_{10}H_{15}NO_2S$	*N*-butyl benzene sulfonamide	MS, ST
23	$C_{18}H_{30}$	tri-*tert*-butylbenzene	MS
24	$C_{16}H_{22}O_4$	diisobutyl phthalate	MS, ST
25	$C_{16}H_{22}O_4$	dibutyl phthalate	MS, ST
26	$C_{24}H_{38}O_4$	diisooctyl phthalate	MS
27	$C_{26}H_{42}O_4$	dioctyl phthalate	MS, ST
28	$C_{24}H_{38}O_4$	dinonyl phthalate	MS
29	$C_{24}H_{38}O_4$	bis(ethylhexyl) phthalate	MS

 * MS: tentatively identified by the library of the equipment, ST: identified with the use of standard substances.

MSD equipment. The minimum percentage of similarity accepted, between the spectra of the sample and from the library, was 90%. For values inferior to 90%, the peak was considered as nonidentified.
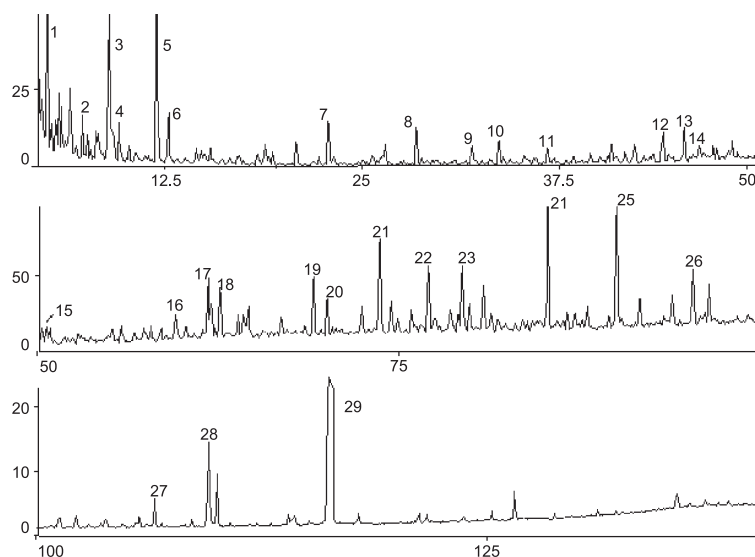

Fig. 1. Total ion chromatogram for the landfill leachate extract. Chromatographic conditions are described in the text.

Table 3
Quantitative analysis of the landfill leachate sample

Compound	Concentration (mg l^{-1})	RSD (%) ($n=3$)
N-ethyl toluene sulfonamide	70.2	12.3
N-butyl benzene sulfonamide	35.6	3.32
Diisobutyl phthalate	65.1	0.75
Dibutyl phthalate	17.9	1.25
Dioctyl phthalate	93.3	1.97

Several nitrogen compounds (nine) and phthalates (six) were identified. Also, one phthalate precursor (compound 16) was found. This compound probably originated from plastic materials and from surfactants. Among the other compounds, some hydrocarbons, alcohols and ketones were also found.

The proposed method has been applied to the quantitative determination of the five compounds above mentioned (standards) in the landfill leachate sample and the results are summarized in Table 3. The results have been calculated on assumption of the percentage recovery of each analyte given on Table 1.

This quantitative analysis may be viewed only as an application of the methodology and not as a characterization of the landfill leachate. The monitoring of a leachate implies in an analysis of a great number of samples and a statistical treatment of data, due the great dependence of the composition of this kind of sample with many external factors, as composition of the residues, climate, season of year, rain, etc.

5. Conclusion

The use of sonication for the recuperation of organic compounds adsorbed at AC, with very small particle size, from aqueous landfill leachate shows good reproducibility, repeatability and high efficiency in the recovery of these compounds. As several well-known substances, such as phthalates, sulfonamides, aromatic hydrocarbons and nitrogen compounds, considered pollutants for the environment, were found, the degree of toxicity of the analyzed landfill leachate is considerable, and it inspires some cares. The developed method can be used in a future monitoring of the quality of the leachate.

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