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Use of Doehlert and constrained mixture designs in the development of a photo-oxidation procedure using UV radiation/H_2O_2 for decomposition of landfill leachate samples and determination of metals by flame atomic absorption spectrometry

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ABSTRACT

This work proposes the use of photo-oxidation degradation with UV radiation/H_2O_2 as sample treatment for the determination of Fe, Zn, Mn, Ni and Co in municipal solid waste landfill leachate by flame atomic absorption spectrometry (FAAS). Three variables (pH, irradiation time and buffer concentration) were optimized using Doehlert design and the proportions of mixture components submitted to UV radiation (leachate sample, buffer solution and H_2O_2 30%, v/v) were optimized using a constrained mixture design. Using the experimental conditions established, this procedure allows limits of detection of 0.075, 0.025, 0.010, 0.075 and 0.041 µg mL^{-1}, and the precision levels expressed as relative standard (%RSD, 0.5 µg mL^{-1}) were 3.6, 1.8, 1.3, 3.3 and 1.7%, for Fe, Mn, Zn, Ni and Co respectively. Recovery tests were carried out for evaluation of the procedure accuracy and recoveries were between 92 and 106% for the studied metals. This procedure has been applied for the analysis of the landfill leachate collected in Jequié, a city of the southwestern region of the State of Bahia, Brazil. The results were compared with those obtained by acid digestion. There was no significant difference between the results obtained by the two methods based on paired t-test at 95% confidence level.

Key words: landfill leachate, photo-oxidation decomposition, UV radiation, metal determination, FAAS.

INTRODUCTION

Municipal solid waste (MSW) landfill is the most widely utilized method of solid waste disposal around the world. Along with its economic advantages, landfills minimize environmental aggression and other drawbacks and allow waste to decompose under controlled conditions. However, the main pollution issue associated with landfill sites is, mainly, the production of liquid leachate. Landfill leachate results from rainfall, runoff of surface drainage and groundwater percolating through the levels of solid waste, extracting the dissolved and suspended materials (Al-Yaqout and Hamoda 2003, Kulikowska and Klimiuk 2008, Manning and Bewsher 1997). It is generally characterized by high concentrations of organic matter and includes toxic and carcinogenic substances such as some metals. It is reported that

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a small amount of landfill leachate can pollute large volumes of groundwater, rendering them unusable. Leachate emissions from landfill sites are of growing concern, primarily due to their toxic impact when released unchecked into the environment, and the potential for landfill sites to generate large volumes of leachate for many decades following closure (Clement et al. 1997, Kjeldsen et al. 2002). Therefore, more attention has been towards researching toxicity of landfill leachate (Guangke et al. 2008).

Due to migration of leachate, soils and ground water of MSW landfill have been contaminated with toxic or potentially toxic (depending on their concentrations) metals such as lead, copper, zinc, chromium, mercury and cadmium; these metals in soils lead to serious environmental problems as they cannot be biodegraded (Hong et al. 2002, Prechthai et al. 2008). The main sources of metals in the dumping sites are garden pesticides, pharmaceuticals, photographic chemicals, certain detergents, personal care products, fluorescent tubes, waste oil, batteries, wood, among others (Slacka et al. 2005, Mohan and Gandhimathi 2009).

Ultraviolet assisted digestion is based on the generation of very reactive species, such as hydroxyl radical (OH•), which can quickly and non-selectively oxidize a broad range of organic substances. Oxidation by H_2O_2 alone has been found ineffective against high concentrations of certain refractory organic matter, due to the low rates of reaction at reasonable H_2O_2 concentrations. Transition metal salts (e.g. iron salts), ozone and UV-light can activate H_2O_2 to form hydroxyl radicals Hung-Yee et al. 2006). Sample treatment using UV irradiation has often been used for sample preparation in the determination of metals employing electroanalytical techniques (Golimowski and Golimowska 1996). However, the use of this radiation in sample treatment for metal determination using spectroanalytical techniques such as FAAS, ICP OES and ICP-MS is still rare. Several reviews have reported fundamentals, advantages, limitations and applications of UV radiation in sample digestion process for inorganic analysis (Capelo-Martínez et al. 2004).

This paper proposes the use of multivariate optimization methodologies (Dohelert and constrained mixture designs) for the development of ultraviolet assisted digestion procedure using H_2O_2 for mineralization of landfill leachate samples collected in a city located in the southwestern region of the State of Bahia, Brazil.

MATERIALS AND METHODS

INSTRUMENTATION

A laboratory-made UV-digester equipped with two 20-W low pressure Mercury lamps was used for the photo-oxidation of the leachate samples.

Measurements for molecular absorption were carried out using an ultraviolet/visible molecular absorption spectrophotometer (PG Instruments, model T-90+).

Metals studied were measured using a flame atomic absorption spectrometer from Perkin Elmer Instruments (Norwalk, CT, EUA) model AAnalyst 200 equipped with an air-acetylene burner. Hollow cathode lamps (Perkin Elmer instruments) were used as light source at a wavelength of 248.33, 213.86, 279.48, 232.00 and 240.73nm and a 0.2, 0.7, 0.2, 0.2 and 0.2 nm spectral bandpass for Fe, Zn, Mn, Ni and Co respectively. Deuterium lamp background correction was also used. The flame composition was acetylene (flow rate: 2.0L min^{-1}) and air (flow rate: 13.5 L min^{-1}). Nebulizer flow rate was 5.0 mL min^{-1}.

REAGENTS AND SOLUTIONS

All reagents were of analytical grade unless otherwise stated. Ultrapure water was obtained from an Elga purification system (Model Purelab Classic). Work solutions of Fe, Zn, Mn, Ni and Co at µg L^{-1} level were prepared by diluting 1000 µg mL^{-1} stock solutions (Merck). Acetate (pH 3.8-5.8), phosphate (5.8-7.5), borate (pH 7.5-9.0) and ammonia (pH 9.0–10.0) buffer solutions were used to adjust the pH of the solutions. Nitric and hydrochloric acid solutions were prepared from the concentrated acids (Merck, Darmstadt, Germany) by dilution with water.

Laboratory glassware was kept overnight in 10% (v/v) nitric acid solution. Before use the glassware was rinsed with deionized water and dried in a dust-free environment.

SAMPLE COLLECTING

Leachate samples were collected from a municipal solid waste landfill located at Jequié`s countryside in the southwestern region of the State of Bahia, Brazil. Polyethylene bottles were used to store leachate samples. Before use the bottles were kept overnight in 10% (v/v) nitric acid solution and rinsed with ultrapure water. Leachate samples were collected directly from the surface of the drain that connects the landfill to the reservoir pool.

PROCEDURES

The optimization procedure for digestion of leachate samples was carried out by Doehlert and constrained mixture designs. Doehlert design was used to optimize the method variables (pH, irradiation time and buffer concentration) and constrained mixture design was used to optimize the proportion among leachate, buffer and hydrogen peroxide volumes. The software Statistica 7.0 was used for the treatment of experimental data. All experiments were carried out in duplicate.

Doehlert design

Method variables to be optimized at this stage were: pH, irradiation time (IT) and buffer concentration (BC). Due to the characteristics of the experimental design matrix used in this study, pH was studied in seven levels, irradiation time in five levels and BC in three levels. The following procedure was followed: a fixed volume (5.0 mL) of leachate was transferred to a Petri dish, and 2 mL of 30% (v/v) hydrogen peroxide and final concentrations between 0.01 and 0.03 mol L^{-1} buffer solution at specific pH was added. The samples were subjected to UV photo-oxidation from 20 to 80 min. The samples were then transferred to a 10mL volumetric flask and diluted to 10 mL. Table I presents all experiments established to the experimental Doehlert matrix for the optimization of these method variables.

Constrained mixture design

Proportions among sample and chemicals for ultra-violet assisted digestion were optimized by using a constrained mixture design. The use of constraints is justified because the presence of three components is always necessary to promote the digestion.

Table IIa presents low and high constraints established for each component and Fig. 1 shows this region. Table IIb presents the experimental matrix for this constrained mixture design. The proportion of each component in each experiment is established by the mixture design matrix used. In this step, method variables such as pH, irradiation time and buffer concentration were fixed at 8.0, 30 minutes and 0.01 mol L^{-1}.

Ultraviolet assisted digestion

After optimization, the ultra-violet assisted digestion must be carried out as follows: a volume of 6.5 mL of leachate is introduced into a Petri dish, and 2.5 mL of 30% (v/v) hydrogen peroxide and 1.0mL of 0.1 mol L^{-1} borate buffer solution are added. The samples are subjected to UV photo-oxidation for 60 min. The samples are then transferred to a 10 mL volumetric flask and diluted to volume with 0.1 mol L^{-1} nitric acid solution.

Acid digestion of leachate samples in hot plate

A volume of 5.0 mL of leachate sample was transferred to a 250 mL Erlenmeyer; 5 mL of

TABLE I
Doehlert matrix for optimization of the leachate digestion procedure based on photo-oxidation assisted by ultraviolet radiation.

Experiment	pH	IT (min)	BC (mol L^{-1})	Absorbance (510 nm)
1	10	35	0.02	0.229
2	10	65	0.02	0.238
3	9	50	0.03	0.319
4	8	35	0.01	0.652
5	8	65	0.01	0.409
6	7	20	0.02	0.708
7	7	50	0.02	0.575/0.555/0.528
8	7	80	0.02	0.496
9	6	35	0.03	0.502
10	6	65	0.03	0.708
11	5	50	0.01	0.618
12	4	35	0.02	0.864
13	4	65	0.02	0.737

IT: irradiation time; BC: buffer concentration.

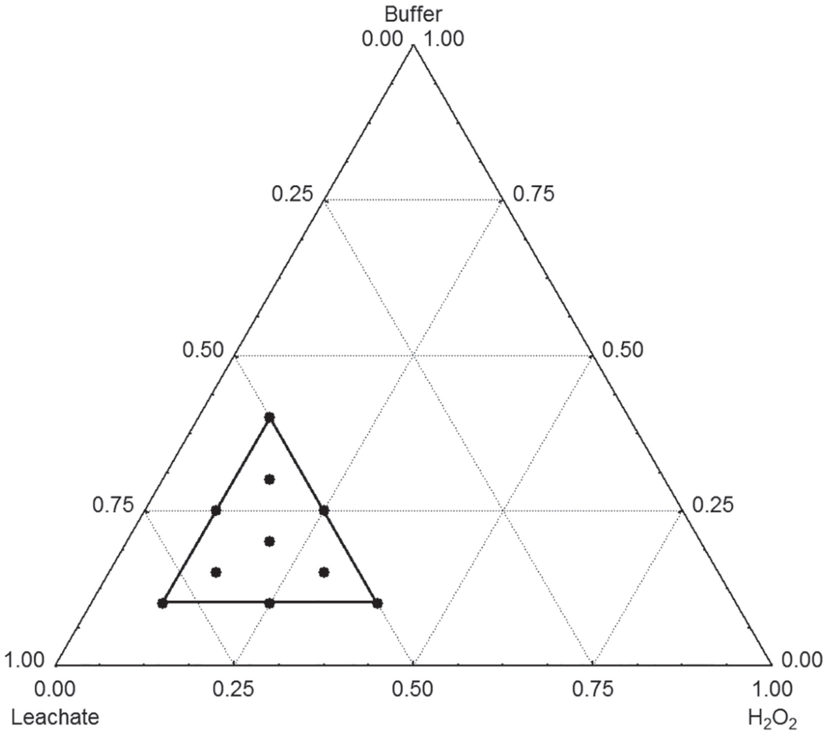

Figure 1 - Experimental region of mixture design delimited by low and high constraints established for each component according to Table IIa.

TABLE II
(a) Low and high constraints for mixture components and (b) experimental matrix applied for optimization of ultraviolet assisted digestion.

(a) Constraints

Mixture Variable	*Low constraint*	*High constraint*
Leachate volume (mL)	5	8
H_2O_2 volume (mL)	1	4
Buffer solution volume (mL)	1	4

(b) Experimental matrix and responses

Exp	*Leachate*	*H_2O_2*	*Buffer*	*Abs*	*Abs/ Leachate volume*
1	8.0	1.0	1.0	0.664/0.649	0.0830/0.0811
2	5.0	4.0	1.0	0.233/0.214	0.0466/0.0428
3	5.0	1.0	4.0	0.194/0.212	0.0388/0.0424
4	5.0	2.5	2.5	0.186/0.210	0.0372/0.0420
5	6.5	1.0	2.5	0.685/0.725	0.1054/0.1115
6	6.5	2.5	1.0	0.356/0.373	0.0548/0.0574
7	6.0	2.0	2.0	0.381/0.342	0.0635/0.0570
8	5.5	1.5	3.0	0.392/0.327	0.0713/0.0595
9	5.5	3.0	1.5	0.284/0.249	0.0516/0.0453
10	7.0	1.5	1.5	0.755/0.629	0.1079/0.0899

concentrated nitric acid and 2 mL of 30% (v/v) hydrogen peroxide were added. Then, samples were heated in hot plate to a complete digestion. The solutions were left to cool down to room temperature, transferred to a calibrated flask and diluted to a final volume of 10 mL with deionized water. Metals were determined in the final solution by flame atomic absorption spectrometry (FAAS).

RESULTS AND DISCUSSION

OPTIMIZATION OF THE PROCEDURE

The performance of ultraviolet assisted digestion depends on some method variables such as pH, buffer concentration irradiation time, among others, as well as proportions of components in the final mixture. Thus, Doehelrt and mixture designs were applied, in order to find the optimum conditions that ensured digested samples with good characteristics. For all experiments sample degradation was monitored measuring the absorbance of the resultant solution at the wavelength of 500 nm. Thus, low absorbances are taken as efficient organic matter degradation.

Doehlert design used, and the found absorbance for each solution obtained in the different experimental conditions, are shown in Table I. Analysis of variance was applied to evaluate the linear and quadratic model fitted to the experimental data. According to ANOVA, the quadratic model showed no lack of fit ($p = 0.1036 > 0.050$) and was chosen for calculating the optimum value.

The quadratic model fitted to the data can be visualized through the response surfaces presented in Figure 2. Results indicate that pH plays an important role in the organic matter degradation using ultraviolet radiation. The lower absorbance is observed when sample's pH solution is close to 10. Irradiation time and buffer concentration, in the studied intervals, do not present effects as significant as pH. Figures 2a and 2b show that, decreases for irradiation time and buffer concentration values, must be accomplished by increase of the pH values.

Thus, the following conditions were selected to carry out the subsequent experiments: irradiation time = 30 min, pH = 10 and final buffer concentration = 0.01 mol L^{-1}.

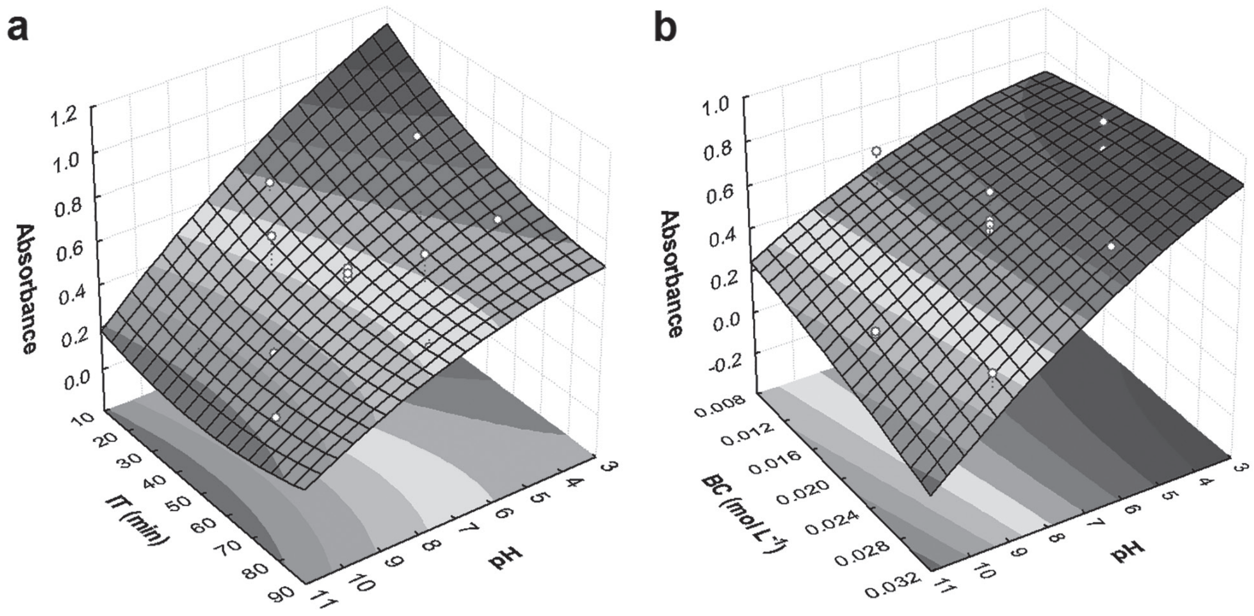

Figure 2 - Response surfaces obtained after to fit a quadratic function in the data presented in Table I. (a) pH versus irradiation time (IT) and (b) pH versus buffer concentration (BC).

A constrained mixture design was used to optimize the proportions of the mixture components (including the sample) submitted to the ultraviolet radiation.

In a mixture design (Ferreira et al. 2007, Bruns et al. 2006) the system properties depend on ingredient proportions, xi, and not on their absolute values. As these proportions are not independent, they must be submitted to Equation 1:

$$\sum_{i=1}^{q} x_i = 1 \text{ for } i = 1, 2, ..., q.$$

It is often of no interest to investigate the entire range of proportion values (0–100%) of the mixture components. Many mixture optimization problems require the presence of all components to form a satisfactory product or the exclusion of experimental regions where it is impossible to obtain a combination for all factors. In these cases, it is convenient to define low and high constraints for some components (Massart et al. 1997, Bezerra et al. 2010).

Table IIb shows the experimental matrix used for this optimization and responses for each experiment that compose it. In order to carry out an adequate evaluation of the response, it was obtained the ratios between absorbance and sample volume. As decrease of sample volume is naturally accomplished by decrease of absorbance, this response treatment was necessary to eliminate this effect.

Figure 3 shows the response surface obtained by fitting a quadratic model to response. The fitted model does not present lack of fit ($p = 0.4488 > 0.050$).

This surface presents a region where the proportions of components presents the minor response. Thus, the optimized proportions for leachate, buffer and hydrogen peroxide in the UV-digestion procedure are 6.5 mL, 1.0 mL and 2.5 mL respectively.

EVALUATION OF MATRIX EFFECT

Matrix effects in techniques based on aspiration/nebulization as FAAS can be originated from differences between transport rates in standards and samples, due to differences of physical properties (viscosity, surface tension, etc.) between them.

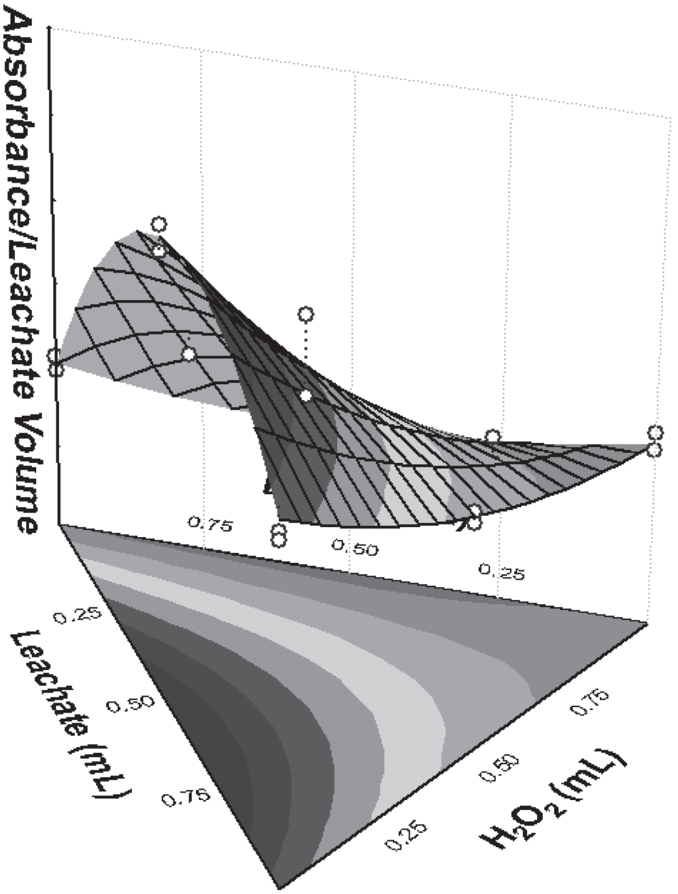

Figure 3 - Response surface obtained after to fit a quadratic function on the data presented in Table II.

Another cause may be the load of organic matter present in the analyzed solution. The amount of energy that can be supplied by the flame for metal liberation from organic matrix, (and also its dissociation and atomization) determines the absorption efficiency of radiation in the analyzed sample. As only free gaseous atoms in the ground state can absorb their characteristic radiation, the sensitivity of FAAS will also depend of load on organic matter present in a solution (Vandecasteele and Block 1993, Skoog et al. 2002). A way to verify the matrix effect on the instrumental signal, is comparing the slopes of analytical curves generated in the presence and absence of matrix. A high organic load, such as that found in landfill leachate, generally causes a decline of slope values.

Initially, the sensitivity of the landfill leachate digestion procedure using UV irradiation for the determination of Fe, Zn, Mn, Ni and Co by FAAS using the analyte addition technique, was compared with the slopes found for aqueous standard solutions. Initially, the sensitivity of the landfill leachate digestion procedure using UV irradiation for the determination of Fe, Zn, Mn, Ni and Co by FAAS using the standard addition technique in the leachate with and without pretreatment, was compared with the slopes found for conventional calibration obtained from aqueous standard solutions (Table III and Figure 4). For all studied metals, analytical curves from aqueous solution present the highest slopes. On the other hand, analytical curves obtained from standard

TABLE III
Comparison among parameters of analytical curves prepared in different medias.

Media	Calibration technique	Equation**	Confidence interval of the slope*	R^2
Fe				
Leachate after UV digestion	Standard addition	y = 0.0612x +0.0231	0.0 604-0.0621	0.9998
Leachate without digestion	Standard addition	y = 0.0535x + 0.0187	0.0524-0.0546	0.9995
Aqueous	Conventional	y = 0.0782x + 0.0032	0.0750-0.0815	0.9987
Buffer and H_2O_2	Conventional	y = 0.0622x + 0.0024	0.0612-0.0632	0.9997
Zn				
Leachate after UV digestion	Standard addition	y = 0.747x + 0.0512	0.719-0.774	0.9993
Leachate without digestion	Standard addition	y = 0.627x + 0.0501	0.609-0.645	0.9996
Aqueous	Conventional	y = 0.786x + 0.0224	0.752-0.819	0.9990
Buffer and H_2O_2	Conventional	y = 0.743x + 0.00452	0.710-0.776	0.9990
Mn				
Leachate after UV digestion	Standard addition	y = 0.152x + 0.459	0.147-0.157	0.9988
Leachate without digestion	Standard addition	y = 0.110x + 0.423	0.106-0.114	0.9984
Aqueous	Conventional	y = 0.158x + 0.00832	0.153-0.164	0.9986
Buffer and H_2O_2	Conventional	y = 0.152x + 0.0196	0.148-0.156	0.9993
Ni				
Leachate after UV digestion	Standard addition	y = 0.0416x + 0.0183	0.0409-0.0424	0.9996
Leachate without digestion	Standard addition	y = 0.0387x + 0.0137	0.0379-0.0395	0.9994
Aqueous	Conventional	y = 0.0422x + 0.00130	0.0410-0.0434	0.9990
Buffer and H_2O_2	Conventional	y = 0.0401x + 0.00124	0.0387-0.0415	0.9985
Co				
Leachate after UV digestion	Standard addition	y = 0.106x + 0.0214	0.103-0.110	0.9985
Leachate without digestion	Standard addition	y = 0.101x + 0.0190	0.0978-0.103	0.9989
Aqueous	Conventional	y = 0.109x + 0.00182	0.106-0.112	0.9992
Buffer and H_2O_2	Conventional	y = 0.108x + 0.00125	0.103-0.113	0.9972

*Confidence level = 95%; **Range of solution concentrations for each added metal: from 0.2 to 2.0 µg mL^{-1}.

addition in the sample without any digestion showed the lowest slopes. Comparisons among the slopes from analytical curves obtained from standard addition on the sample with and without UV digestion reveal that, at a 95% confidence level, there are significant differences among them. However, analyzing the confidence intervals from slopes among the calibration curves obtained from digested sample by UV radiation and the aqueous solution containing the same buffer amounts, it is observed that they are very similar. These results demonstrate that the proposed digestion using UV irradiation is efficient for leachate degradation and for the determination of the studied metals by FAAS, and that the quantification of these metals can be made using standards in buffer media for calibration.

Analytical Features of Procedure

The limits of detection and quantification were determined according to IUPAC recommendations (Royal Society of Chemistry Analytical Methods Committee 1994, Miller and Miller 2005). Considering a 6.5 mL volume of digested sample, limits of detection of 0.075, 0.025, 0.010, 0.075 and 0.041 µg mL-1, limits of quantification of 0.25; 0.081; 0.033; 0.25 and 0.14 g mL-1 and precision levels expressed as relative standard (%RSD, 0.5 µg mL-1) of 3.6, 1.8, 1.3, 3.3 and 1.7%, were obtained for Fe, Mn, Zn, Ni and Co, respectively.

Addition/recovery tests were performed for evaluation of the accuracy as no appropriate certified reference materials are available

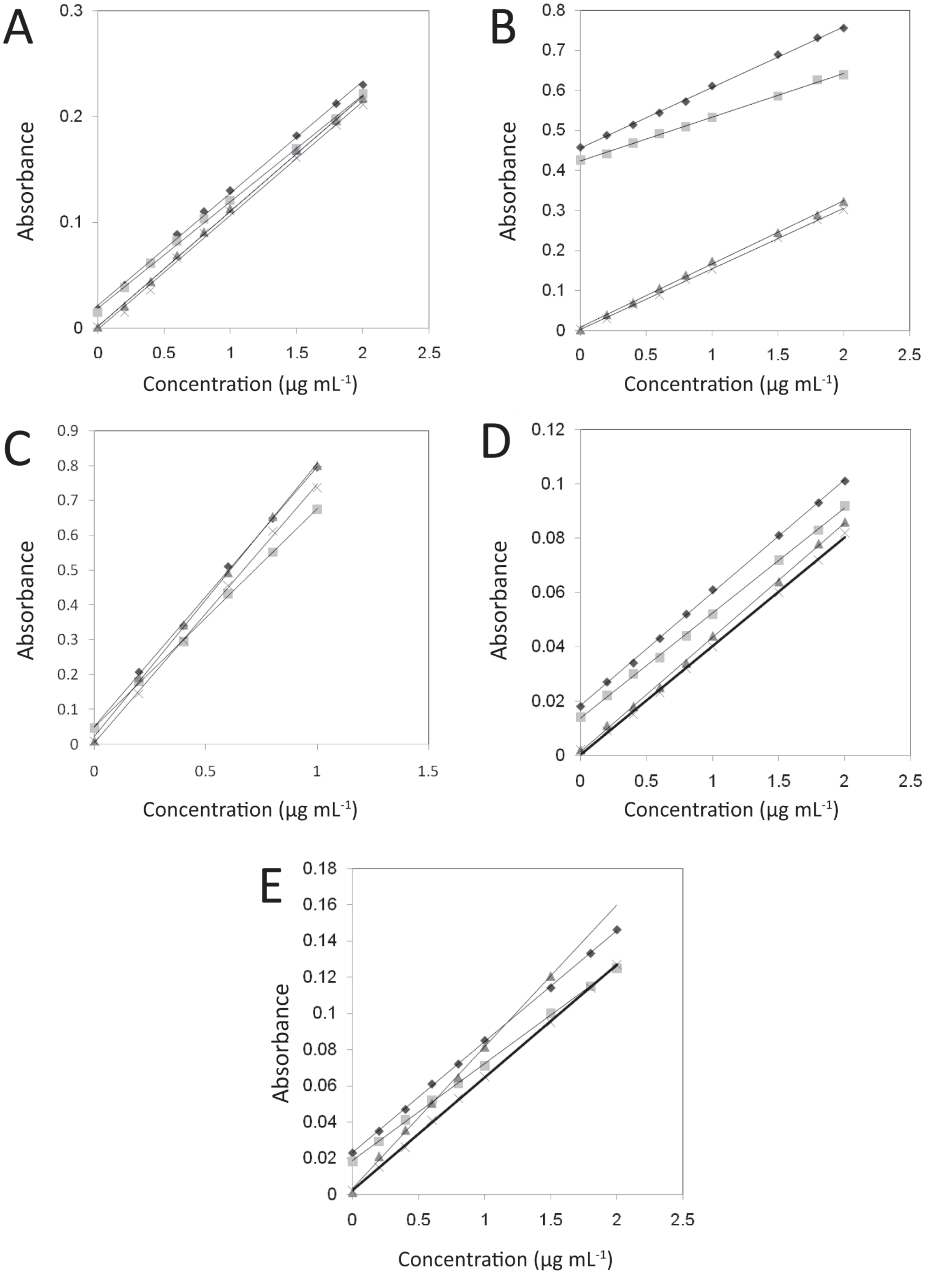

Figure 4 - Analytical curves in different medias: (♦) leachate sample after UV digestion; (□) leachate without digestion (Δ) aqueous solution and (X) aqueous solution of buffer. (**A**) Cobalt; (**B**) manganese; (**C**) zinc; (**D**) nickel and (**E**) iron.

for leachate. Results are presented in Table IV. Recoveries found, ranged from 92 to 106% for the studied metals.

Application

The proposed UV digestion procedure was used for the determination of Fe, Zn, Mn, Ni and Co in municipal solid waste landfill leachate samples using FAAS. Additionally, results for the sample collected in May 2011 were compared with those obtained after an acid digestion also using FAAS. Results are shown in Table IV. A statistical evaluation of these results, using a paired *t*-test in a confidence level of 95%, demonstrates that there are no significant differences between the two digestion procedures based on results for studied metals.

TABLE IV
Metal content (µg mL^{-1}, N=3) and recovery test (%) in leachate samples collected in different months in the municipal landfill of Jequié-Bahia-Brazil.

	Fe		**Mn**		**Zn**		**Ni**		**Co**	
	Found	Recovery	Found	Recovery	Found	Recovery	Found	Recovery	Found	Recovery
Dec/2010	0.66 ± 0.01	-	3.35 ± 0.04	-	0.290 ± 0.03	-	0.77 ± 0.04	-	0.39 ± 0.02	-
Jan/2011	0.70 ± 0.06	-	3.94 ± 0.06	-	0.230 ± 0.01	-	0.58 ± 0.09	-	0.39 ± 0.01	-
Feb/2011	0.90 ± 0.06	-	0.13 ± 0.01	-	0.120 ± 0.01	-	1.50 ± 0.04	-	0.51 ± 0.01	-
Mar/2011	0.46 ± 0.03	-	1.67 ± 0.02	-	0.120 ± 0.02	-	0.95 ± 0.04	-	0.45 ± 0.02	-
May/2011	1.81 ± 0.05	-	2.51 ± 0.02	-	0.19 ± 0.02	-	1.20 ± 0.09	-	0.73 ± 0.02	-
+ 0.5 (0.769)	2.52 ± 0.05	92	3.22 ± 0.03	92	0.93 ± 0.01	96	1.95 ± 0.03	98	1.45 ± 0.06	94
+1.0 (1.538)	3.44 ± 0.04	106	4.11 ± 0.02	104	1.65 ± 0.02	95	2.72 ± 0.03	99	2.27 ± 0.04	100
May/2011*	1.86 ± 0.06	-	2.55 ± 0.05	-	0.20 ± 0.02	-	1.96 ± 0.05	-	0.74 ± 0.03	-
Pared t-test (Hot plate and UV Digestion for sample collected on May 2011)										
Calculated F-values	0.8065	-	0.1967	-	0.9231	-	0.3553	-	0.3871	-
Critic F	0.1053	-	0.1053		0.1053		0.1053		0.1053	

*Digestion in hot plate methodology.

CONCLUSIONS

The proposed procedure was a simple and efficient alternative for pretreatment of municipal solid waste landfill leachate samples for the determination of Fe, Zn, Mn, Ni and Co by FAAS.

An advantage of this procedure is the digestion process that results in a weak alkaline solution, which can be ideal for analyses where pre-concentration procedures have to be performed after the digestion step.

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RESUMO

Este trabalho propõe o uso de degradação por foto-oxidação com radiação ultravioleta e H_2O_2 como técnica de tratamento de amostras para a determinação de Fe, Zn, Mn, Ni e Co a partir de chorume de aterro sanitário municipal usando espectrometria de absorção atômica com chama (FAAS). Três variáveis (pH, tempo de irradiação e concentração de tampão) foram otimizadas usando planejamento Doehlert e as proporções dos componentes da mistura submetida à irradiação ultravioleta (chorume, solução tampão e H_2O_2 30% v/v) foram otimizadas usando-se um planejamento de misturas com restrições. Usando as condições experimentais estabelecidas, este procedimento forneceu limites de detecção de 0,075; 0,025; 0,010; 0,075 e 0,041 µg mL^{-1}, e os níveis de precisão, expressos como desvio padrão relativo (%RSD, 0,5 µg mL^{-1}) foram 3,6; 1,8; 1,3; 3,3 e

1,7% pra Fe, Mn, Zn, Ni e Co respectivamente. Testes de recuperação foram realizados para avaliação da exatidão do procedimento e as recuperações encontradas estavam entre 92 e 106% para os metais estudados. Este procedimento foi aplicado nas amostras de chorume coletadas no município de Jequié, região sudoeste da Bahia, Brasil. Os resultados foram comparados com aqueles obtidos pelo procedimento de digestão em meio ácido. Não houve diferenças significativas entre os resultados obtidos nos dois métodos com base no teste t-pareado a um nível de confiança de 95%.

Palavras-chave: chorume, decomposição por foto oxidação, radiação UV, determinação de metais, FAAS.

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