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Talanta 68 (2005) 165–170
Talanta
www.elsevier.com/locate/talanta

Application of sequential injection–square wave voltammetry (SI–SWV) to study the adsorption of atrazine onto a tropical soil sample

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Received 15 April 2005; received in revised form 23 May 2005; accepted 23 May 2005
Available online 11 July 2005

Abstract

Square wave voltammetry automated by sequential injection analysis was applied to determine the Freundlich adsorption coefficients for the adsorption of atrazine onto a clay rich soil. The detection limit in soil extracts was between 0.18 and 0.48 μmol L^{-1}, depending on the medium used to prepare the extracts (0.010 mol L^{-1} KCl, $CaCl_2$ or HNO_3 and 0.0050 mol L^{-1} H_2SO_4), all of them conditioned in 40 mmol L^{-1} Britton–Robinson buffer at pH 2.0 in presence of 0.25 mol L^{-1} $NaNO_3$. Also in soil extracts the linear dynamic range was between 1.16 and 18.5 μmol L^{-1} (0.25–4.0 μg mL^{-1}), with a sampling frequency of 190 h^{-1}. The K_f Freundlich adsorption coefficient was 3.8 ± 0.2 $\mu mol^{1-1/n}$ L^n kg^{-1} in medium of 0.010 mol L^{-1} KCl or $CaCl_2$, but increased to 7.7 ± 0.1 and 9.0 ± 0.3 $\mu mol^{1-1/n}$ L^n kg^{-1} in 0.010 mol L^{-1} HNO_3 and 0.0050 mol L^{-1} H_2SO_4, respectively. The increase of K_f was related to the decrease of pH from 6.4–6.7 in KCl and $CaCl_2$ to 3.7–4.0 in presence of HNO_3 or H_2SO_4, which favors protonation of atrazine, facilitating electrostatic attractions with negative charges of the clay components of the soil. The $1/n$ parameters were between 0.76 and 0.86, indicating that the isotherms are not linear, suggesting the occurrence of chemisorption at specific adsorption sites. No statistically significant differences were observed in comparison to the adsorption coefficients obtained by HPLC. The advantage of the proposed SI–SWV method is the great saving of reagent because it does not use organic solvent as in the case of HPLC (50% (v/v) acetonitrile in the mobile phase). Additionally the start up of SI–SWV is immediate (no column conditioning necessary) and the analysis time is only 19 s.

Keywords: Sequential injection; Square wave voltammetry; Atrazine; Adsorption; Soil

1. Introduction

Triazines have been used in diverse crops as herbicides and, nowadays, atrazine and simazine are among the pre- and post-emergence herbicides most used around the world [1]. After application the herbicide can be adsorbed in soil components such as clays and natural organic matter (NOM), having a significant decrease in their effectiveness. Adsorption of atrazine to soils is directly related to the content of organic matter and humidity [2]. Because triazines are weakly basic substances, they can be protonated in acidic soils, interacting with negative charges of clays and NOM [3]. Such interactions decrease the concentration of triazines in the soluble fractions of the soil, decreasing the geochemical mobility of the herbicide. Despite of these interactions, a great concern about triazines is their runoff to ground waters and surface waters [4]. Atrazine and simazine, as well as their metabolites, are the herbicides most often detected in natural waters [4–6].

The geochemical mobility and the potential runoff of herbicides to natural waters can be evaluated by adsorption isotherms obtained with the soil under study, using different conditions of pH, ionic strength and chemical composition of the aqueous phase [7]. Adsorption isotherms can be obtained by the batch approach, in which a constant mass of soil is equilibrated with a wide range of herbicide concentrations, using a constant total volume of soil suspension for each assay. After the equilibrium is reached, the soil is separated, and the residual concentration of the herbicide in the

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doi:10.1016/j.talanta.2005.05.025

aqueous phase is determined by an appropriate analytical method, which should be fast and sensitive, having a wide linear dynamic range. Additionally, because a large number of samples are generated to construct the isotherms, the analytical method should have low cost, low consumption of sample and reagents and, as a consequence, low generation of residues.

Triazines are commonly determined by gas chromatography with the nitrogen–phosphorus detector (NPD) [8], flame ionization detector (FID) [9] and mass spectrometry (MS) [10]. Other analytical techniques used for atrazine determination are the high performance chromatography (HPLC) with UV detection [11], immunoassay [12] and electroanalytical techniques, especially pulse voltammetry with different kinds of working electrodes [13–15].

The use of electroanalytical techniques for determination of herbicides has increased, but only few cases describe their application in adsorption studies [14,16]. A drawback of batch electroanalytical methods that use the hanging mercury drop electrode (HMDE) is the low sampling frequency, which is a consequence of the need of cell changing and cleaning between each determination. To overcome this limitation several flow devices [17] have been coupled to the capillary of the HMDE, enabling the use of this electrode under continuous flow [18] or flow injection and sequential analysis [19]. This paper describes the application of a sequential injection–square wave voltammetry (SI–SWV) method [19] using the HMDE to study the adsorption of atrazine onto a tropical soil sample, under distinct conditions of pH and ionic strength. The results and the proposed method were evaluated in comparison with the performance of an HPLC method for determination of atrazine.

2. Experimental

2.1. Apparatus and reagents

Voltammetric measurements were carried out using an EG&G PAR model 263A potentiostat. An EG&G PAR model 303A static mercury drop electrode (SMDE) was used in all experiments. The flow cell adapted to the Hg capillary was already described in the literature [18]. The electrochemical cell was completed with an Ag/AgCl reference electrode (KCl saturated) and a platinum auxiliary electrode. A Metrohm 654 pH-meter was used with a Mettler Toledo HA405-60-88G-S7/120—Ag/AgCl combination glass electrode for pH measurements. Ultrapure N_2 (O_2 <2 ppm) was used to remove dissolved O_2 from the solutions and to provide an inert atmosphere inside the cell. Purified and doubly distilled mercury was used in the working electrode.

A Fialab 3500 (FIAlab Instruments, USA, Bellevue, WA) instrument was used in all experiments in the sequential injection mode according to Fig. 1. Solutions were driven by a 5.00 mL syringe pump and an eight port rotary valve, RV (Valco Instrument Co., Houston, TX). The holding coil, HC, was made of 3 m × 0.8 mm i.d. Teflon (polytetrafluoroethylene, PTFE) tubing. The tubing connecting RV to the flow cell was 27 cm long, made of 0.5 mm i.d. PTFE tubing. All other tubing connections were made of 0.5 mm i.d. PTFE tubing and PTFE nuts and ferrules (Upchurch, Oak Harbor, WA). An auxiliary peristaltic pump (not shown in Fig. 1) was used to continuously draw off the excess of solution inside the glass three-electrode cell, as described previously [18].

An LC 9A Shimadzu high performance liquid chromatograph (HPLC), equipped with a SPD 6 AV UV detector, and the LC Workstation Class-LC 10 software was used in all experiments for quantification of atrazine. A SB C-18 Zorbax—HP column (3.5 μm, 150 mm × 4.6 mm) connected to a C-18 Phenomenex guard column was used. Sample injection was made with a rotary Rheodyne valve using a 20 μL sample loop.

All reagents used in this work were of analytical grade and all working solutions were prepared in deionized water (Simplicity 185 system from Millipore coupled to an UV lamp) A stock 20 μg mL^{-1} atrazine (AT) was prepared dissolving the solid standard (Riedel-de Haën, purity >99%, molar mass of 215.69 g mol^{-1}) in deionized water. Working solutions were prepared by diluting this stock solution in distilled deionized water. The voltammetric experiments were performed in medium of 40 mmol L^{-1} Britton–Robinson (BR) buffer of pH 2.0 in presence of 0.25 mol L $NaNO_3$. The BR buffer was prepared from a mixture of phosphoric acid (pK_a 2.14, 7.20 and 12.15), acetic acid (pK_a 4.75) and boric acid (pK_a 9.24, 12.74 and 13.80), with all components at concentration of 40 mmol L^{-1}. The pH of the BR buffer was monitored with combination glass electrode and adjusted to 2.0 by adding NaOH solution.

2.2. Soil sample

The soil sample was collected at the experimental farm of the Escola Superior de Agricultura Luiz de Queiroz da Universidade de São Paulo (ESALQ-USP) in the Piracicaba municipality, São Paulo state, Brazil, in a 500 m^2 area with no history of application of herbicides. Fifteen surface samples were collected at depths between 0 and 20 cm from four different points and mixed to form a composed sample. The soil was air-dried and gently ground with a pestle and mortar to pass in a 1.0 mm sieve. The sieved sample was further dried in a vacuum oven at 35 °C until constant weight, a process that required approximately 48 h, and finally stored in a desiccator. The CHN composition was: 1.58 ± 0.04% C; 0.76 ± 0.04% H; 0.07 ± 0.01% N. Sand, silt and clay contents were 29, 18 and 53%, respectively. Kaolinite is the dominant clay in this soil, with some contributions of sesquioxides [20].

2.3. Adsorption experiments

A mass of 1.000 g (±1 mg) of the dried soil was transferred to polypropylene centrifuge tubes (Corning) with capacity of 10 mL. A volume of 50 μL of 1.0 mol L^{-1} KCl, or

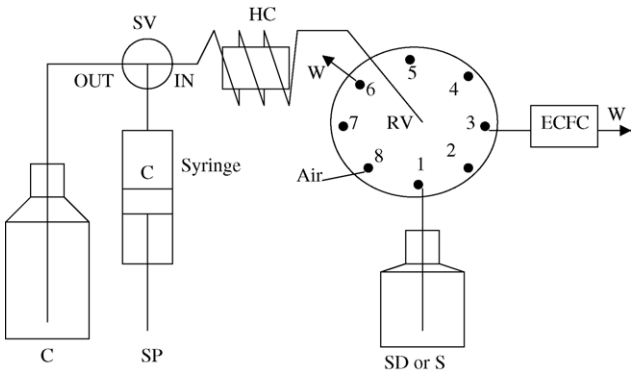

Fig. 1. Sequential injection manifold to perform SI–SWV. C: carrier (40 mmol L^{-1} BR buffer, pH 2.0, in 0.25 mol L^{-1} $NaNO_3$); SV: syringe valve; SP: syringe pump; HC: holding coil (made of 3 m of PTFE tubing of 0.8 mm internal diameter); RV: eight port rotary selection valve; SD or S: standard or sample reservoir; ECFC: electrochemical flow cell (connection between ECFC and RV is made of 0.27 m of PTFE tubing of 0.5 mm i.d.); W: waste. More details about the ECFC are given in Ref [18].

1.0 mol L^{-1} $CaCl_2$, or 1.0 mol L^{-1} HNO_3, or 0.50 mol L^{-1} H_2SO_4 was added to each tube, followed by a suitable volume of a 20 μg mL^{-1} (92.7 μmol L^{-1}) atrazine stock solution to provide initial atrazine concentrations of 0.25, 0.50, 1.00, 2.00, 4.00, 6.00, 8.00 and 10.0 μg mL^{-1} after completing the total solution volume to 5.00 mL with deionized water. All centrifuge tubes were sealed, protected from light and shaken in a thermostated orbital shaker for 24 h at 25.0 ± 0.1 °C. The contact time of 24 h was previously determined to allow the system to reach the chemical equilibrium [21,22]. After equilibration the solid phases were let to decant and the supernatant solution was filtered through 0.45 μm cellulose acetate membranes. A volume of 2.50 mL of this solution was pipetted and properly conditioned for square wave voltammetry measurements by adding 2.50 mL of 80 mmol L^{-1} BR buffer (pH 2.0) in 0.50 mol L^{-1} $NaNO_3$.

2.4. Standards in soil extracts

To correct for matrix effects, calibration of the system was made in soil extracts prepared in the same medium used to perform the adsorption experiments. To prepare the standard solutions in the matrix solution, a mass of 10.0 g of soil was equilibrated with 49.50 mL of deionized water plus 0.50 mL of 1.0 mol L^{-1} $CaCl_2$, or 1.0 mol L^{-1} KCl, or 1.0 mol L^{-1} HNO_3, or 0.50 mol L^{-1} H_2SO_4. This extraction was performed for 24 h in a thermostated orbital shaker programmed at 25.0 ± 0.1 °C. After extraction, the solid phases were let to decant and the supernatant solution was filtered through 0.45 μm cellulose acetate membranes. Standard solutions of atrazine with concentrations 0.060, 0.10, 0.25, 0.50, 1.0, 2.0 and 4.0 μg mL^{-1} were prepared by diluting suitable volumes of a 10.0 μg mL^{-1} stock atrazine solution (prepared in 80 mmol L^{-1} BR buffer and 0.50 mol L^{-1} $NaNO_3$) in 2.50 mL of the filtered soil extract, completing to 5.00 mL with appropriate volumes of 80 mmol L^{-1} BR buffer in 0.50 mol L^{-1} $NaNO_3$. For comparison, another set of standard solutions was prepared in the 40 mmol L^{-1} BR buffer (pH 2.0) in 0.25 mol L^{-1} $NaNO_3$ using only deionized water.

2.5. Determination of the free concentrations of atrazine

The first step of the SIA program was to fill HC and the electrochemical cell (Fig. 1) with the carrier solution (40 mmol L^{-1} BR buffer in presence of 0.25 mol L^{-1} $NaNO_3$). The tubing connecting the port 1 of RV was filled with standard or sample solutions (SD or S). The potentiostat and the SIA programs were started simultaneously [19]. The potentiostat is programmed with a delay time of 19 s before scanning the potential to allow the SIA system to perform aspiration of carrier into the syringe and the appropriate sample volume to the holding coil: while this time runs, with SV at position "OUT" (Fig. 1) the syringe pump aspirated 800 μL of C inside the syringe at a flow rate of 500 μL s^{-1}. Next, with SV at position "IN", 100 μL of air and 500 μL of standard/sample solution were sequentially aspirated to HC at 50 μL s^{-1} from ports 8 and 1 of RV, respectively. Then, RV switched to port 3 and SP dispensed 400 μL of standard/sample toward the flow cell at 50 μL s^{-1}, while the potentiostat scanned the potential from −0.5 to −1.2 V using the frequency of 300 Hz and pulse height of 25 mV. The excess of sample/standard solution and the air bubble were expelled from HC dispensing 500 μL through port 6 of RV. Finally, RV switched back to port 3 and SP emptied the syringe at 100 μL s^{-1} washing the system for the next sample.

If necessary, the sample solutions were diluted with the solution composed by 50% (v/v) soil extract in 40 mmol L^{-1} BR buffer and 0.25 mol L^{-1} $NaNO_3$.

2.6. HPLC analysis

The HPLC analyses were carried out using an isocratic elution mode with a mobile phase constituted by 50% (v/v) 2.5 mmol L^{-1} ammonium acetate–acetic acid buffer (pH 4.5) and 50% (v/v) acetonitrile. Both solutions constituting the mobile phase were previously filtered through 0.45 μm PTFE membranes. Helium was used as degassing gas in all experiments. The analyses were performed under a flow rate of 1.0 mL min^{-1}. Under these analytical conditions, the atrazine retention time is close to 4.2 min. The UV detector monitored the absorbance at 220 nm [15].

2.7. Data treatment

Sorption data were treated by the linearized Freundlich equation:

$$\log(q) = \log K_f + \frac{1}{n} \log C \quad (1)$$

where q is the concentration of the studied compound in the solid phase (μmol kg^{-1}), C the solution concentration

(μmol L^{-1}) after a given contact time (24 h in the present study), and K_f and $1/n$ are the empirical constants related to sorption.

3. Results and discussion

3.1. Analytical curves

The analytical experimental parameters used in the present work are based on the development of the SI–SWV method for determination of atrazine in spiked river water samples described previously [19]. An optimization of the flow rate and square wave frequency in the medium of 50% (v/v) soil extracts in 40 mmol L^{-1} BR buffer at pH 2.0 and 0.25 mol L^{-1} $NaNO_3$ lead to optimal values of 50 μL s^{-1} and 300 Hz, in agreement with the optimal conditions previously found in solutions prepared with deionized water [19].

Table 1 shows the statistical parameters of the analytical curves obtained in the several media in which the adsorption isotherms were obtained. The linear dynamic range in solutions prepared using only deionized water was between 0.1 and 1.0 μg mL^{-1}, but for solutions prepared in 50% (v/v) soil extract the linear dynamic range was between 0.25 and 4.0 μg mL^{-1}. The relative standard deviations for the 0.010 mol L^{-1} $CaCl_2$ soil extract solutions with atrazine concentrations of 0.25 and 2.0 μg mL^{-1} were 5.7 and 1.3%, respectively (10 measurements), denoting a good repeatability for the measurements. The relative standard deviation of the slope and intercept of analytical curves obtained in five different working days did not exceed 4%, and the magnitude of this deviation was mostly dependent on the positioning of the flow cell in the Hg capillary when the system was assembled [18].

The best sensitivity was found for strong acid solutions in medium prepared with deionized water. This behavior may be related to a greater extension of atrazine protonation (pK_a 1.71) in these media because one proton is involved in the rate-determining step of the reduction process, as previously described by Vaz et al. [14] and dos Santos et al. [15].

The slope of the analytical curves decreased significantly for the solutions prepared with 50% (v/v) soil extract (Table 1). This behavior may be related to interactions of atrazine with extracted soil components such as complex colloidal species of Fe and Al oxyhydroxides, which might slow down the electron transfer rate between the electrode and the atrazine molecules. The interaction of atrazine with soil solution components is also evidenced by the switch of peak potentials from −860 mV in solutions prepared with deionized water to −890 mV in presence of the soil extract. The switch of peak potentials to values 30 mV more negative is related to an extra energy necessary for reduction of atrazine at the Hg electrode, giving support to the hypothesis of interaction of atrazine with soil components in the extract. Another possibility is the interaction of the extractable soil species with the Hg surface, resulting in a decrease of the electron transfer rates. Castanho et al. [16] also observed a decrease in the slope of the analytical curve prepared in soil suspensions for determination of methyl parathion by differential pulse polarography, but the authors attributed the fact to the presence of contaminants in the soil solution. Because of the significant differences between the slopes of the analytical curves in soil extracts and deionized water, the Freundlich adsorption coefficients were obtained by computing the free atrazine concentrations using the calibration curves obtained in soil extracts.

3.2. Adsorption experiments

Fig. 2 shows the adsorption isotherms obtained by the proposed SI–SWV method in comparison to the curves obtained by HPLC analysis of free atrazine in the adsorption solutions. Adsorption data were represented by L-type isotherms, which were properly fitted by the Freundlich equation ($r^2 > 0.998$) using linear regression analysis to calculate the K_f and $1/n$ values (Table 2). The *t*-test revealed that there are no evidences of systematic differences between the adsorption coefficient values obtained by SI–SWV and HPLC.

The $1/n$ coefficient in all situations was between 0.76 and 0.86, suggesting that adsorption occurs predominantly in specific binding sites, rather than following the partition model, for which a $1/n$ value much closer to 1 would be expected.

Table 1
Statistical parameters (±standard deviations) for typical analytical curves obtained by SI–SWV deionized water and soil extract, both in presence of 40 mmol L^{-1} BR buffer at pH 2.0 and 0.25 mol L^{-1} $NaNO_3$

Medium	Deionized water[a]				Soil extract[b]			
	Slope (nA L μmol^{-1})	Intercept (nA)	r^2	LOD/LOQ[c] (μmol L^{-1})	Slope (nA L μmol^{-1})	Intercept (nA)	r^2	LOD/LOQ (μmol L^{-1})
0.010 mol L^{-1} KCl	−410 ± 7	26 ± 20	0.9993	0.17/0.57	−273 ± 6	63 ± 31	0.9991	0.39/1.1
0.010 mol L^{-1} $CaCl_2$	−503 ± 5	70 ± 15	0.9998	0.11/0.35	−267 ± 6	31 ± 29	0.9990	0.48/1.0
0.010 mol L^{-1} HNO_3	−560 ± 15	25 ± 20	0.9993	0.13/0.44	−301 ± 3	39 ± 16	0.9998	0.18/0.60
0.005 mol L^{-1} H_2SO_4	−609 ± 11	57 ± 15	0.9993	0.10/0.31	−310 ± 5	110 ± 27	0.9995	0.30/1.0

Limit of detection (LOD) and limit of quantification (LOQ) are also shown.
[a] Statistical parameters valid for the concentration range between 0.060 and 1.0 μg mL^{-1} (0.28–4.64 μmol L^{-1}) atrazine.
[b] Statistical parameters valid for the concentration range between 0.25 and 4.0 μg mL^{-1} (1.16–18.5 μmol L^{-1}) atrazine.
[c] LOD and LOQ were computed from $3s_{y/x}$ and $10s_{y/x}$, respectively, where $s_{y/x}$ is the standard deviation of *y*-residuals [27].

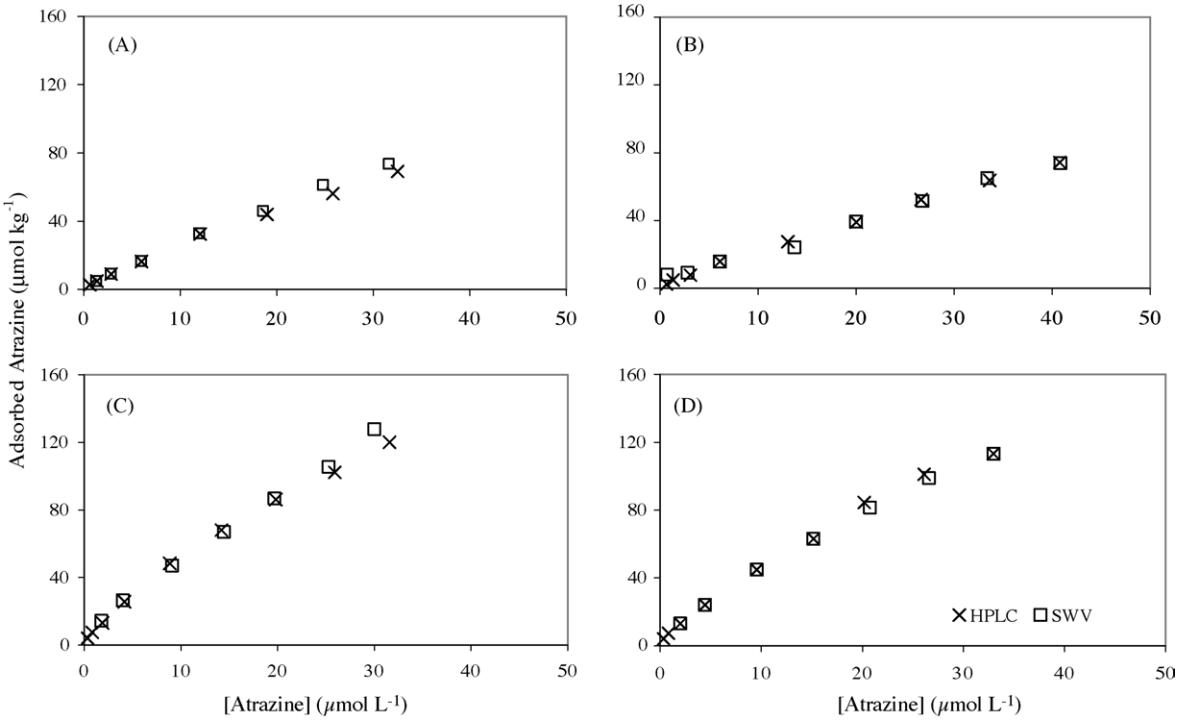

Fig. 2. Adsorption isotherms obtained by SI–SWV proposed method (□) and by HPLC (×) in medium of 0.010 mol L^{-1} KCl (A), 0.010 mol L^{-1} $CaCl_2$, (B) 0.010 mol L^{-1} HNO_3 (C) and 0.0050 mol L^{-1} H_2SO_4 (D).

Adsorption of atrazine is stronger in acidic medium (mean values K_f of 9.0 ± 0.3 and 7.7 ± 0.1 $\mu mol^{1-1/n}\ L^{1/n}\ kg^{-1}$ in 0.010 mol L^{-1} HNO_3 and 0.0050 mol L^{-1} H_2SO_4, respectively) than in medium of $CaCl_2$ and KCl, both of them showing K_f values of 3.8 ± 0.2 $\mu mol^{1-1/n}\ L^{1/n}\ kg^{-1}$. The K_f values are strongly related to the proton intensity of the suspension after the contact time, that is, the larger K_f were found in medium of lower pH (Table 2). Such a behavior is related to protonation of atrazine and electrostatic attractions with the permanent negative charges of clays. The K_f and $1/n$ adsorption coefficients found in the present work are in reasonable agreement with the parameters reported for other soils with similar contents of clays, organic carbon and pH [21,23,24].

Because the soil studied has a low content of organic matter, the adsorption process is predominantly governed by interaction of atrazine with the mineral phases of the soil, especially clay minerals. Kaolinite is the major clay component in the studied soil, with significant concentration of sesquioxides. Kaolinite crystals in Brazilian soils contain high concentrations of Fe, and are generally poorly crystalline [25]. Much of this Fe is probably substituting for Al in the octahedral sheet, a composition that favors the formation of protonated atrazine in the interlayer water due to the hydrolysis of the trivalent cations, enhancing the adsorption by electrostatic interactions between the protonated atrazine and negative charges in the soil surface, as proposed by Herwig et al. [26]. This hypothesis is supported by the enhancement of adsorption in medium with higher proton intensities, as observed in the present work.

3.3. Evaluation of the analytical methods

The major advantages of the proposed SI–SWV over HPLC are the low consumption of reagent and the short

Table 2
Mean (±standard errors) Freundlich K_f ($\mu mol^{1-1/n}\ L^{1/n}\ kg^{-1}$) and $1/n$ parameters for adsorption of atrazine onto a tropical soil sample obtained by SI–SWV and HPLC

Medium	SI–SWV			HPLC			t_{K_f}[a]	$t_{1/n}$[a]	pH[b]
	K_f	$1/n$	r^2	K_f	$1/n$	r^2			
10 mmol L^{-1} KCl	3.8 ± 0.2[c]	0.86 ± 0.01	0.999	3.9 ± 0.1	0.83 ± 0.01	0.999	0.40	2.53	6.7
10 mmol L^{-1} $CaCl_2$	3.8 ± 0.2	0.79 ± 0.02	0.998	3.8 ± 0.2	0.79 ± 0.02	0.999	0.06	0.18	6.4
10 mmol L^{-1} HNO_3	9.0 ± 0.3	0.76 ± 0.01	0.998	8.7 ± 0.2	0.76 ± 0.01	0.999	1.11	0.06	3.7
5 mmol L^{-1} H_2SO_4	7.7 ± 0.1	0.77 ± 0.01	0.9997	8.2 ± 0.3	0.76 ± 0.01	0.998	2.06	1.28	4.0

[a] The critical t value for 2 degrees of freedom at the 95% confidence level is 4.30 [27].
[b] pH measured after 24 h of equilibration with soil.
[c] Results are average of duplicate of adsorption experiments.

time of analysis. In the HPLC method a consumption of 2.1 mL of acetonitrile per analysis can be estimated because the retention time of atrazine is 4.2 min and the flow rate of the mobile phase (consisted by 50% (v/v) of acetonitrile) is 1.0 mL min^{-1}. Additionally, the HPLC method requires near 30 min of column conditioning before starting up the serial analyses, which requires approximately 15 mL of acetonitrile at the flow rate of 1.0 mL min^{-1}. The SI–SWV method does not require conditioning and use of organic solvent. The start up is immediate, with consumption of 400 μL of sample and 800 μL of carrier per analysis. The time of analysis in SI–SWV is 19 s, implying in a sampling frequency of 190 h^{-1}. On the other hand, the HPLC method is more sensitive, having a detection limit of 0.8 μg L^{-1} (3.7×10^{-9} mol L^{-1}) [22] and can be calibrated with standards prepared in deionized water. No significant differences in retention times were observed for pure atrazine standards and solutions resulting from the adsorption study, suggesting that under the HPLC conditions, atrazine is dissociated from the solution soil components during the elution. This fact may be explained by the interactions with the C18 column and with the mobile phase.

4. Conclusion

The proposed SI–SWV method was suitable for determination of free atrazine concentrations in soil extracts, allowing the construction of adsorption isotherms to be accomplished with short times of analyses and low consumption of reagents. The Freundlich adsorption coefficients obtained by the proposed method did not differ from the coefficients obtained by HPLC, a technique that is widely used to evaluate adsorption properties of herbicides to soil samples. The proposed method can be exploited to investigate adsorption properties of several other herbicides and pesticides because most of them are electroactive, or can be derivatized to electroactive forms.

Acknowledgements

Authors are grateful to CNPq and FAPESP for financial support and fellowships.

References

[1] M. Graymore, F. Stagnitti, G. Allinson, Environ. Int. 26 (2001) 483.
[2] A. Walker, Pest. Sci. 3 (1972) 139.
[3] J.B. Weber, C.J. Peter, Weed Sci. 30 (1982) 14.
[4] M.A. Townsend, D.P. Young, Int. J. Environ. Anal. Chem. 78 (2000) 9.
[5] V. Laabs, W. Amelung, A. Pinto, A. Altstaedt, W. Zech, Chemosphere 41 (2000) 1441.
[6] M.J. Shiptalo, L.B. Owens, Environ. Sci. Technol. 37 (2003) 944.
[7] M.B. McBride, Environmental Chemistry of Soils, Oxford University Press, New York, 1994.
[8] R. Eisert, K. Levsen, Fresenius J. Anal. Chem. 351 (1995) 555.
[9] J. Dalluge, T. Hankemeier, R.J.J. Vreuls, U.A.T. Brinkman, J. Chromatogr. A 830 (1999) 377.
[10] H. Sabik, B. Rondeau, P. Gagnon, R. Jeannot, K. Dohrendorf, Int. J. Environ. Anal. Chem. 83 (2003) 457.
[11] M. Berg, R.S. Muller, R.P. Schwarzenbach, Anal. Chem. 67 (1995) 1860.
[12] M.A. Nelson, A. Gates, M. Dodlinger, D.S. Hage, Anal. Chem. 76 (2004) 805.
[13] S. Morais, O. Tavares, P.C. Batista-Paiga, C. Delerue-Matos, Anal. Lett. 37 (2004) 3271.
[14] C.M.P. Vaz, S. Crestana, S.A.S. Machado, L.H. Mazo, L.A. Avaca, Int. J. Environ. Anal. Chem. 62 (1996) 65.
[15] L.B.O. dos Santos, G. Abate, J.C. Masini, Talanta 62 (2004) 667.
[16] G.M. Castanho, C.M.P. Vaz, S.A.S. Machado, J. Braz. Chem. Soc. 14 (2003) 594.
[17] A. Cavicchioli, D. Daniel, I.G.R. Gutz, Electroanalysis 16 (2004) 391.
[18] G. Abate, J. Lichtig, J.C. Masini, Talanta 58 (2002) 433.
[19] L.B.O. dos Santos, M.S.P. Silva, J.C. Masini, Anal. Chim. Acta 528 (2005) 21.
[20] J.A. Melfi, C.R. Montes, A. Carvalho, An. Acad. Bras. Cienc. 76 (2004) 139.
[21] S. Fingler, S. Stipicevic, V. Drevenkar, Int. J. Environ. Anal. Chem. 84 (2004) 83.
[22] G. Abate, J.C. Penteado, J.D. Cuzzi, G.C. Vitti, J. Lichtig, J.C. Masini, J. Agric. Food Chem. 52 (2004) 6747.
[23] B.M. Gawlik, A. Lamberty, J. Pauwels, W.E.H. Blum, A. Mentler, B. Bussian, O. Eklo, K. Fox, W. Kordel, D. Henecke, T. Maurer, C. Perrin-Ganier, J. Pfungmacher, E. Romero-Taboada, G. Szabo, H. Muntau, Sci. Total Environ. 312 (2003) 23.
[24] T.B. Moorman, K. Jayachandran, A. Reungsang, Soil Sci. 166 (2001) 921.
[25] V.F. Melo, B. Singh, C.E.G.R. Schaefer, R.F. Novais, M.P.F. Fontes, Soil Sci. Soc. Am. J. 65 (2001) 1324.
[26] U. Herwig, E. Klumpp, H. Narres, M.J. Schuger, Appl. Clay Sci. 18 (2001) 211.
[27] J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, 2nd ed., Ellis Horwood Limited, Chichester, 1988.