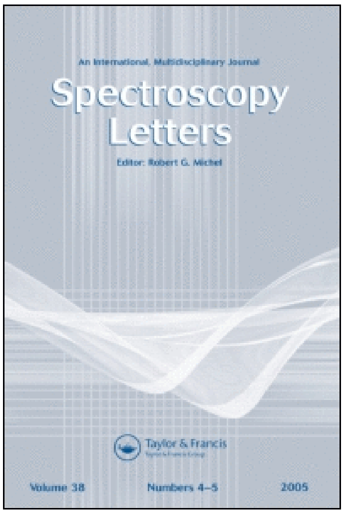

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Development of a Spectrophotometric Sequential Injection Methodology for Online Monitoring of the Adsorption of Paraquat on Clay Mineral and Soil

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Development of a Spectrophotometric Sequential Injection Methodology for Online Monitoring of the Adsorption of Paraquat on Clay Mineral and Soil

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Abstract: The reduction of paraquat by sodium dithionite in alkaline solution was explored to develop an automated, spectrophotometric, sequential injection method for online determination of the herbicide in suspensions of solid adsorbents. A tangential filter was used for interfacing the suspension and the analyzer. The linear dynamic range was between 0.1 and 20 mg L^{-1}, with detection and quantification limits of 0.039 and 0.10 mg L^{-1}, respectively. Sampling throughput was 102 hr^{-1}. Precision at the 5 mg L^{-1} paraquat concentration was 2.9%, with a consumption of dithionite of 1 mg per analysis. The method revealed that adsorption of paraquat onto vermiculite is faster and quantitative in comparison with a tropical soil.

Keywords: Adsorption kinetics, clays, paraquat, sequential injection, sodium dithionite, soil

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INTRODUCTION

Paraquat (1,1′-dimethyl-4,4′-bypiridilium ion) is a defoliant and desiccant agent used to control herbal growth in terrestrial and aquatic environments. It is considered toxic for algae, fish, and other organisms, including humans. The adverse effects caused by chronical and acute exposures to this herbicide are well-known, and cases of death by casual ingestion or poisoning are documented in the literature.[1]

Once paraquat enters the soil environment, it is rapidly and strongly bound to soil components such as clay minerals and organic matter,[2] but even so, there have been many authenticated cases of the detection of its residuals in water sources.[3,4] For removal of paraquat from water and wastewater, two principal treatments are used: advanced oxidative processes (AOPs)[5] and adsorptive processes on porous solids such as granular activated carbon.[6] An important feature of cationic paraquat is to adsorb strongly on clay minerals and somewhat less on activated carbon.[7] Retention by adsorption at solid–liquid interface depends on the medium composition, which may also affect the adsorption kinetics. The evaluation of kinetic and thermodynamic adsorption parameters are made by batch experiments in which known amounts of adsorbate are placed in contact with the adsorbent by selected time intervals, followed by phase separation and quantification of the adsorbate in the aqueous solutions.[2,7,8] Although this approach allows one to evaluate the sorption kinetics of slow sorption reactions, it lacks temporal resolution for fast surface reactions, so that real-time monitoring of the free concentrations would be necessary in these cases.

Sequential injection analysis (SIA) was proposed as a robust single-channel flow technique that would attend the requirements for industrial process control, with minimal needs for maintenance and recalibration.[9] Additionally, the system is designed to perform different liquid handling processes with minimal mechanical reconfiguration. Operations such as online filtration, in-line reactions, dilution, preconcentration, and standard additions have been described, as reviewed by Lenehan et al.[10] Monitoring adsorption processes require separation of the solid phase, a task that can be accomplished by online filtration using tangential filters coupled to the SIA system, as has been previously described in the real-time monitoring of nutrients and metabolites in bioprocesses.[11]

In the current paper, we describe the development of a spectrophotometric sequential injection method for online monitoring of the sorption of paraquat on the clay mineral vermiculite and on a typical Brazilian tropical soil. The regulatory concentration level for paraquat in drinking water is 3 μg L^{-1} (U.S. EPA), which is much lower than the 39 μg L^{-1} obtained in this work, but the objective was not to develop the method for monitoring drinking water but rather to study the adsorption process. Thus, this work is not placed in the context of the regulatory level, which, to be attained, needs a preconcentration step before analysis.

MATERIALS AND METHODS

Reagents

The tetrahydrate dichloride salt of paraquat (CAS 1910-42-5) was purchased from ChemService Inc (West Chester, PA, USA) with purity of 99%. The paraquat working solutions were prepared with deionized water by appropriate dilution of a 1000 mg L^{-1} stock solution. All other reagents used in this work were of analytical grade from Sigma-Aldrich (Sâo Paulo, SP, Brazil), or Merck (Rio de Janeiro, RJ, Brazil).

The colorimetric reagent was composed by 0.50% (m/v) sodium dithionite (CAS 7775-14-6) solution prepared with deionized water free of dissolved O_2 in presence of 0.10 mol L^{-1} borate buffer (pH 9.0). Because this reagent is unstable, a fresh solution was prepared at intervals of 2 hr. The carrier solution was a 0.10 mol L^{-1} borate buffer (pH 9.0) solution.

Apparatus

A Fialab 3500 (FIAlab Instruments, Bellevue, WA, USA) 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, USA). The holding coil (HC) was made of 3 m of 0.8-mm-i.d. Teflon (polytetrafluoroethylene, PTFE) tubing. The reaction coil (RC) was 50-cm long, made of 0.8-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, USA). A Micronal B382 spectrophotometer (Micronal, São Paulo, SP, Brazil) was used as detector with a Hellma U-flow cell with 10-mm light pathlength and 80-μL internal volume. The control of the pump and valve was made with the Fialab 3500 software. Acquisition data was performed with a PC-LPM-16 National Instruments board (National Instruments, Austin, TX, USA).

An Alitea C4V peristaltic pump (FIAlab Instruments, Bellevue, WA, USA), PP, fitted out with Tygon pump tubing of 2.79 mm i.d., was used to continuously pump the suspension through an A-SEP tangential filter (TF) from Applikon (Applikon Analytical, Schiedam, The Netherlands) at a flow rate of 6.7 mL min^{-1}. Filtration was performed with 0.45-μm cellulose acetate membranes 47 mm in diameter. The outlet tube of filtered solution was connected to port 5 of the rotary selection valve of the SIA system.

Procedure for Calibration

All the following procedures are based on the flow diagram shown in Fig. 1. First, HC, RC, and the spectrophotometric flow cell were filled with carrier

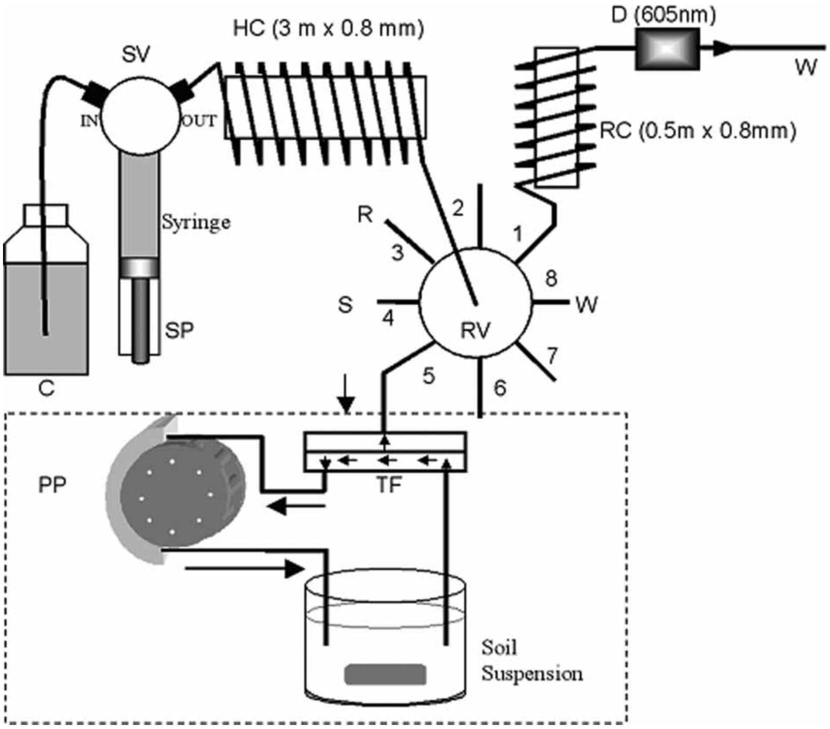


Figure 1. Sequential injection system for online monitoring the sorption of paraquat. C, carrier solution; SV, syringe valve; SP, syringe pump; HC, holding coil; RV, eight-port rotary selection valve; S, standard solution; R, 0.50% (m/v) sodium dithionite reagent; RC, reaction coil; D, spectrophotometric detector; W, waste; TF, tangential filter; PP, peristaltic pump.

solution. The tubing connecting reagent reservoir and the sampling line to the RV were filled with the respective solutions. All other tubing connected to unused ports of RV were filled with carrier solution to avoid entrance of air bubbles in the system. The spectrophotometer was set at 605 nm.

To start the automatic analyses, the syringe valve is set at position IN and the syringe pump aspirates 4500 μL of carrier solution inside the syringe at a flow rate of 300 $\mu L\ s^{-1}$. Next, the syringe valve switches to position OUT and, with the rotary valve at positions 3 or 4, the syringe pump stacks sequentially 100 μL of the reagent R (port 3), 200 μL of standard S (port 4), and 100 μL of reagent R (port 3) inside the holding coil using a flow rate of 150 $\mu L\ s^{-1}$. In the final step, the rotary valve switches to port 1 and the syringe pump dispenses 2500 μL of carrier at a flow rate of 400 $\mu L\ s^{-1}$, injecting the mixture zone through the mixing coil and the flow cell of the detector. Next, the flow rate is increased to 450 $\mu L\ s^{-1}$ and the syringe is emptied, flushing the system for the next analysis. As the sample zone travels from the holding coil to the detector, it overlaps with the reagent zone and the buffer carrier by axial and radial dispersion, leading to the formation of the reaction product. The procedure is repeated three times for each sample/standard. Standard paraquat solutions with concentrations between 0.10 and 20.0 mg L^{-1} were used for construction of the analytical curve using the maximum peak height provided by the data acquisition software as the analytical signal.

Procedure for Online Monitoring

For studying the sorption kinetic, the components showed inside the dotted line of Fig. 1 are used. An aliquot of 100 mL of 20 mg L^{-1} paraquat solution was transferred to a 250-mL beaker. The solution was vigorously stirred and the peristaltic pump (PP) was activated, pumping the solution through the tangential filter back to the beaker. The outlet of the tangential filter is connected to port 5 of the rotary valve. To fill the tubing connecting the outlet of the tangential filter to the rotary valve with representative solution flowing through the closed loop, the following steps are performed: with the syringe valve at position IN, the syringe pump aspirates 4500 μL of carrier inside the syringe at 300 μL s^{-1}. The syringe valve switches to position OUT and the rotary valve to position 5. After that, the syringe pump aspirates 300 μL of filtered sample inside the holding coil at a flow rate of 100 μL s^{-1}. The excess of sample is flushed from the system with 1500 μL of carrier at a flow rate of 300 μL s^{-1} through port 8 of the rotary valve (auxiliary waste). The rotary valve turns to position 3 and the syringe pump aspirates, sequentially, 100 μL of reagent (port 3), 200 μL of the filtered sample (port 5), and 100 μL of reagent (port 3) into the holding coil, at a flow rate of 150 μL s^{-1}. Finally, the rotary valve switches to position 1 and the syringe pump dispenses 2500 μL at a flow rate of 400 μL s^{-1}, injecting the reaction zone toward the detector flow cell (D). Finally, the flow rate is increased to 450 μL s^{-1}, and the syringe pump empties the syringe, flushing the system for the next analysis. To start the kinetic measurements, a mass of 100 mg of the soil sample or clay mineral is added to the paraquat solution and, simultaneously, the SIA system starts performing sampling and analysis of paraquat in the filtered solution.

RESULTS AND DISCUSSION

Influence of the Physical Parameters

The first parameter studied was the sample volume, which was varied from 100 to 400 μL, sandwiched between two 100-μL plugs of the 0.50% (m/v) sodium dithionite reagent. The absorbance read at the peak maximum increased up to the sample volume of 300 μL, decaying significantly when 400 μL was used, even with the dispersion coefficient approaching unity. This fact is caused by lack of interpenetration between the sample and reagent zones, leading to regions of the sample zone in which the reagent concentration is not at the appropriate stoichiometric excess. The signal obtained from the reaction between 300 μL of a 4.0 mg L^{-1} paraquat and 0.50% (m/v) sodium dithionite reached a maximum when the reaction zone was formed by two 100-μL reagent zones sandwiching the sample zone. Reagent volumes larger than 100 μL lead to elements of reagent zones that do not interpenetrate with sample zone, causing only increase in the dispersion and waste of reagent.[12]

The residence time was studied by varying the reaction coil length and the flow rate. The length of the reaction coil was increased from 25 to 300 cm (Fig. 2A) showing that the analytical signal for a 3.0 mg L^{-1} paraquat solution is almost constant for coil lengths between 25 and 100 cm, with a peak maximum for the reaction coil of 50 cm, which was used in further studies. The influence of the flow rate on the analytical signal was studied in the range between 50 and 500 μL s^{-1} during the injection of the mixture zone toward the detector. The analytical signal increased up to the flow rate of 400 μL s^{-1}, remaining approximately constant at 500 μL s^{-1} (Fig. 2B). A 120-s stopped flow time started just after the solution elements corresponding with the peak maximum had reached the flow cell showed that the reaction is completely developed using either flow rates of 75 or 400 μL s^{-1} (Fig. 2C). The small decrease of absorbance observed in Fig. 2C may be assigned to dispersion by axial diffusion because a similar profile was observed using bromothymol blue and borate buffer instead of paraquat and dithionite solutions. This observation confirms that under the experimental conditions, the reduction of paraquat stops at the blue cation radical ($Pq^{+}\bullet$) without significant formation of the uncolored dihydrobipyridyl species (Pq)[13] (see Scheme 1).

The molecular absorption spectrum of the blue cation radical ($Pq\bullet^{+}$) is shown in Fig. 3, exhibiting a maximum in the visible range at 605 nm, which was chosen to perform the absorbance measurements.

Composition of the Carrier and Reagent Concentration

To minimize the Schlieren effect caused by the gradient of refraction indexes, the approach of matching the carrier and reagent compositions was used.[14] Thus, the sodium dithionite reagent and the carrier were prepared in 0.10 mol L^{-1} borate buffer at pH 9.0, which was also chosen because the borate/boric acid solution has an optimal buffering capacity at pH 9.0, and no significant variation of the analytical signals was observed between pH 8.0 and 11.0.

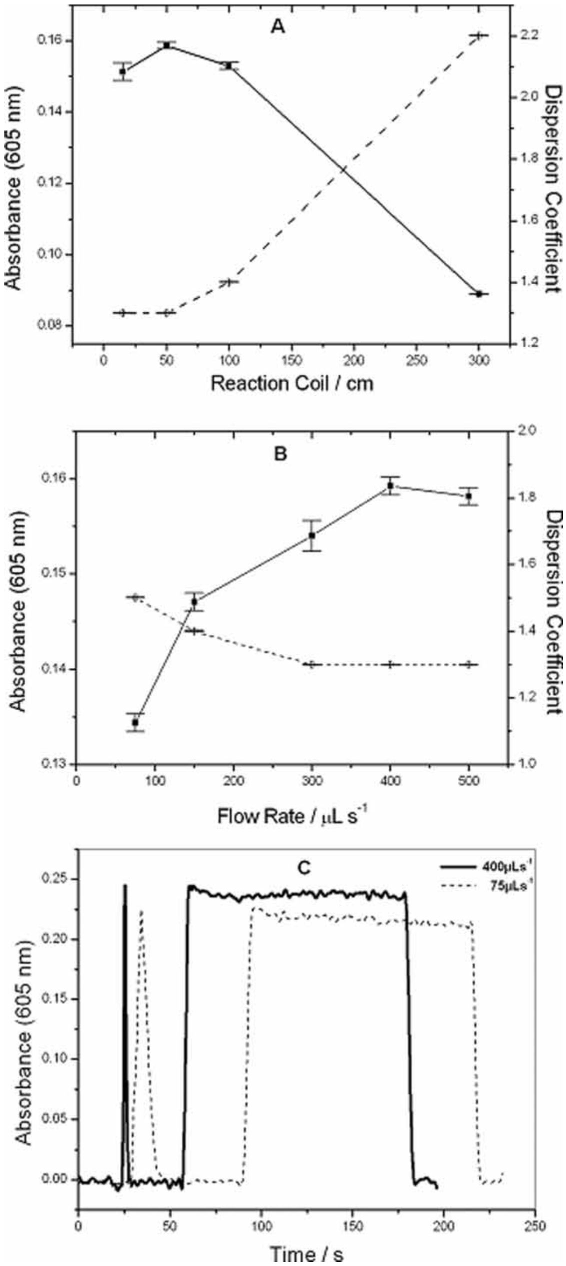
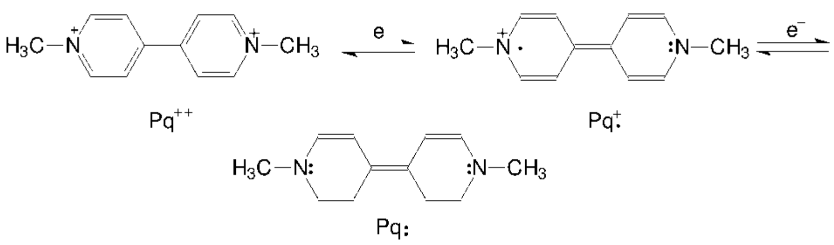


Figure 2. Influence of the residence time on the analytical signal and dispersion coefficient. The residence time was studied by varying (A) the reaction coil length, (B) the flow rate, as well as by (C) stopping the flow rate for 120 s when the reaction zone corresponding with the peak maximum reached the flow cell. The experiment was performed with a 5.0 mg L^{-1} paraquat solution.



Scheme 1. Reduction steps of paraquat cation ($P_{q^{2+}}$).

The concentration of sodium dithionite was studied in the range between 0.25% and 10% (m/v) using the sequence previously determined, that is, aspirating 300 μL of 3.0 mg L^{-1} paraquat standard sandwiched between two 100-μL plugs of reagent and injecting the mixture zone toward the detector at a flow rate of 400 μL s^{-1}. For an 0.25 (m/v) sodium dithionite reagent, the absorbance read at the peak maximum was 0.126 ± 0.010, but increasing the reagent concentration by a factor of 5, from 0.50% to 2.5% (m/v) caused an increase of the peak absorbance from 0.149 ± 0.005 to 0.187 ± 0.005, that is, an increase

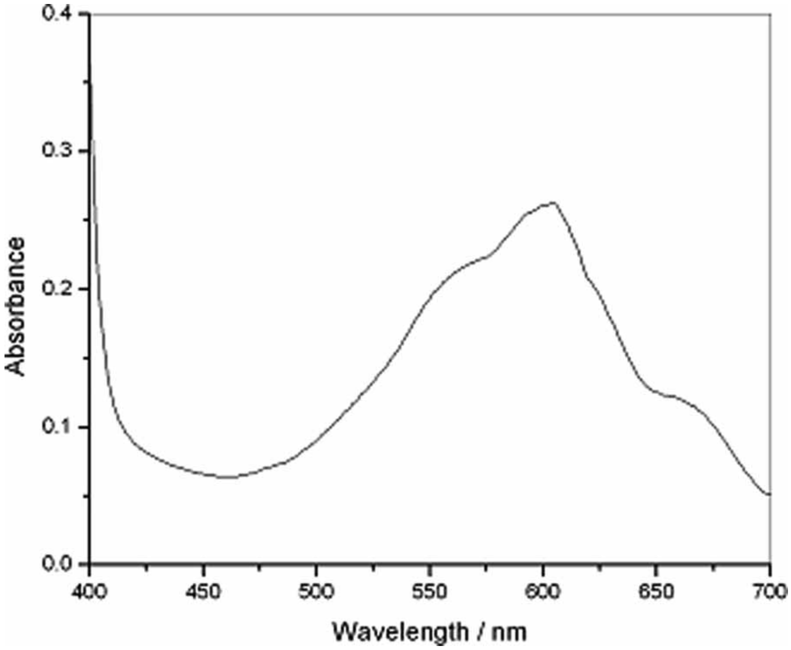


Figure 3. Molecular absorption spectrum of the blue paraquat radical cation obtained from the reaction of a 5.0 × 10^{-5} mol L^{-1} paraquat solution with 0.50% (m/v) sodium dithionite in medium of 0.10 mol L^{-1} borate buffer (pH 9.0).

by a factor of only 1.25. Because the sodium dithionite reagent is unstable and has to be prepared at intervals of 2 hr, we opted to work with the 0.50% (m/v) concentration to minimize the waste of reagent.

Figures of Merit and Analytical Curves

The limit of detection (LOD) was investigated by injecting paraquat solutions at concentrations of 0.050, 0.080, 0.10, 0.20, and 0.50 mg L^{-1}, in addition to the blank solution constituted by deionized water (Fig. 4). The LOD was computed

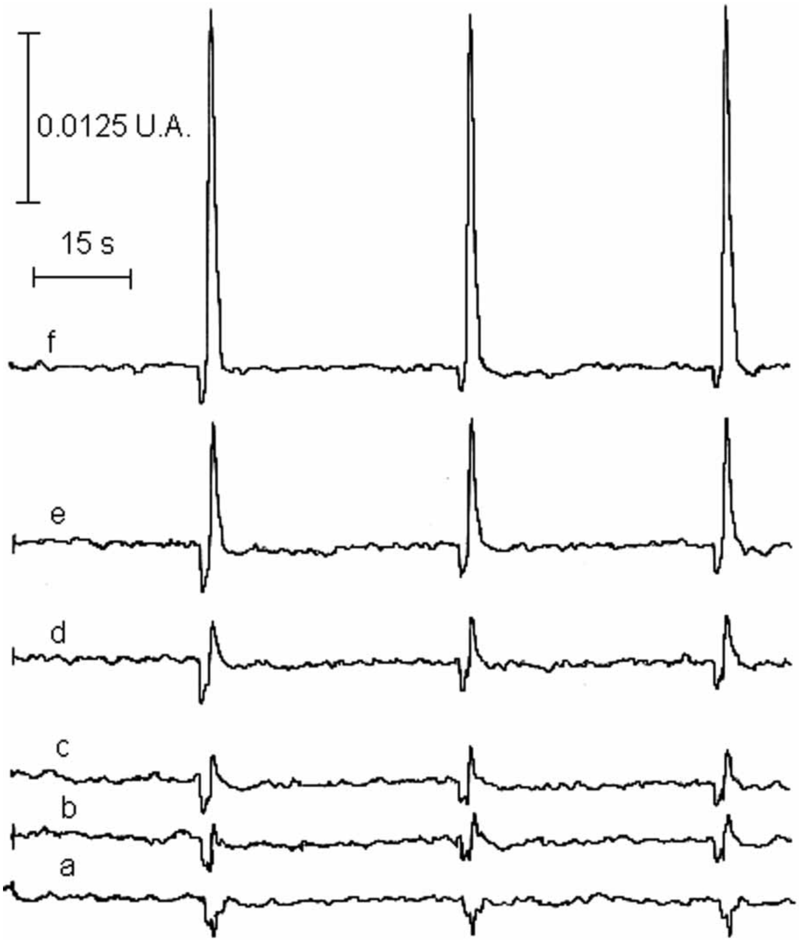


Figure 4. Investigation on the limit of detection, performed by injecting triplicate of (a) blank solution, (b) 0.050, (c) 0.080, (d) 0.10, (e) 0.20, and (f) 0.50 mg L^{-1} paraquat solutions.

by the relation LOD $= 3\,S_b/m$, where S_b is the standard deviation of 10 measurements of peak absorbance of the blank solution, and m is the slope of the analytical curve, resulting in the value of 0.039 mg L^{-1}. The limit of quantification (LOQ) was considered 0.10 mg L^{-1}, which is the first point of the linear range of the analytical curve. Both LOD and LOQ were of the same magnitude of other spectrophotometric methods based on flow injection systems.[15–17]

The linear dynamic range can be extended up to 20.0 mg L^{-1} paraquat solutions and, in the range of paraquat concentrations between 0.10 and 20 mg L^{-1}, the calibration curve fitted to the equation $A_{605} = (0.0551 \pm 0.0005)\,C_{Pq^{2+}} - (0.010 \pm 0.004)$ with correlation coefficient of 0.9996 and with the slope given in units of L mg^{-1}. The relative standard deviation (RSD) of the slope of the analytical curves obtained with different preparations of the sodium dithionite reagent (at intervals of 2 hr) was less than 5%. Ten repetitive injections of a 5.0 mg L^{-1} paraquat solution gave an RSD of 2.9%. The consumption of the sodium dithionite reagent was 1 mg per analysis. Including the online filtration and washing, the sampling throughput was 102 hr^{-1}, implying that kinetic measurements can be made at intervals of 35 s.

Monitoring the Sorption Kinetic of Paraquat

Figure 5 shows that paraquat concentrations ($C_{Pq^{2+}}$) follow first-order exponential decay in suspensions of both soil and vermiculite particles. In soil, the experimental data fitted the equation

$$C_{Pq^{2+}} = (10.84 \pm 0.05) + (9.0 \pm 0.1)e^{[-t/(89 \pm 3)]}, \text{ with } r^2 = 0.998.$$

For the vermiculite suspension, the experimental data fitted the equation

$$C_{Pq^{2+}} = (19 \pm 1)e^{[-t/(45 \pm 2)]}, \text{ with } r^2 = 0.92.$$

From these plots, it is clear that adsorption onto the vermiculite particles is much faster than in soil. Additionally, when the system soil–paraquat solution approaches the equilibrium, more than 50% of the initial paraquat concentration is still remaining in solution, implying in potential mobility of this herbicide in soils. In the vermiculite suspension, it is possible to estimate a $t_{1/2}$ value of 29 s for 50% decay in the initial paraquat concentration. Additionally, at the end of the experiment ($t > 500$s), the solution concentrations of paraquat were less than LOQ (0.10 mg L^{-1}), implying an adsorption of more than 99.5% of the initial paraquat present in the suspension. One of the major differences that can explain the faster and more efficient adsorption of paraquat on vermiculite is the total surface areas, which are 379 $m^2\,g^{-1}$ for vermiculite and 49.3 $m^2\,g^{-1}$ for the soil. Additionally, the cation exchange capacities are 185 and 1170 mmol kg^{-1} for the soil and vermiculite samples, respectively.[18,19] This means that for the same mass of solid material, there is a much greater number of cation exchange sites in

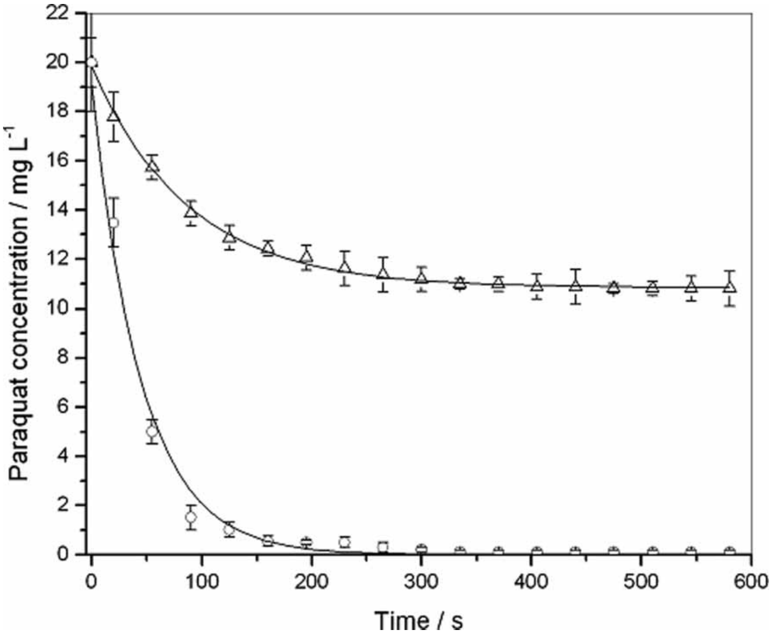


Figure 5. Online monitoring of adsorption kinetics of paraquat from 100 mL of a 20.0 mg L^{-1} solution (initial concentration) on a suspension containing 100 mg of soil (Δ) or vermiculite (○).

the vermiculite than in the soil sample, a fact that can also explain the faster and quantitative adsorption of paraquat on the clay mineral suspension.

CONCLUSIONS

This paper demonstrates that the high temporal resolution provided by the spectrophotometric sequential injection system, associated with the tangential filter, enables the investigation of the kinetic behavior in adsorption systems with much greater detail than usually provided by the batch approach. This can be useful for environmental scientists elaborating models to describe dispersion profile of herbicides in soils and waters and may provide useful information for the development of solid materials aimed at the removal of pollutants from waters.

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