



Development and calibration of an electrolytic cell for ion determination in a soil solution

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ABSTRACT. An electrolytic cell was developed to monitor soil modifications after crop fertigation with wastewaters from agroindustrial plants. The device was first calibrated with different levels of potassium chloride dissolved in aqueous solutions at various temperatures. Nernst's model was used to fit the voltage indicated from the electrolytic cell versus the ionic activity of the potassium from the aqueous solutions of electrical conductivity and known ionic concentrations and the diluted wastewater samples. The equipment accurately indicated the tensions after appropriated correction of the electrical current and the temperature. The device estimated with accuracy the ionic coefficient of activity, the concentration of the potassium chloride and the concentration of the ion K dissolved in the agro-industrial wastewater.

Keywords: ionic activity, potassium, wastewater, fertigation.

Desenvolvimento e calibração de um equipamento para determinação da concentração de íons na solução do solo

RESUMO. Uma célula eletrolítica foi desenvolvida para monitorar as modificações do solo após a fertirrigação de culturas com águas residuárias agroindustriais. Neste primeiro passo, o dispositivo fabricado foi calibrado utilizando diferentes níveis de cloreto de potássio dissolvido em soluções aquosas sob várias temperaturas. O modelo de Nernst foi utilizado para ajustar a tensão indicada a partir da célula eletrolítica versus a atividade iônica do potássio a partir de soluções aquosas de condutividade elétrica e concentração iônica conhecidas e amostras de águas residuárias diluídas. O equipamento indicou com precisão as tensões após a correção apropriada tanto da corrente elétrica como da temperatura. O dispositivo estimou com precisão o coeficiente de atividade iônica, a concentração do cloreto de potássio e a concentração do íon K dissolvido nas águas residuárias agroindustriais.

Palavras-chave: atividade iônica, potássio, água residuária, fertirrigação.

Introduction

The storage, maintenance and treatment of waste water from agro-industrial plants in large ponds have become expensive. Environmental contamination frequently occurs and it has been necessary to find an appropriate disposal for these specific wastes. The alternative recommendation as a source for fertigation and plant nutrient (JIMENEZ-CISNEROS, 1995; TOZE, 2006; HEIDARPOUR et al., 2007; LEAL et al., 2009; QADIR et al., 2010; PEREIRA et al., 2011) during the dry season has been facing serious difficulties due to the incipient concern on the effects of the various ions leaching into the tropical soil profile (HARRIS; URIE, 1983; JALALI et al., 2008; KOLAHCHI; JALALI, 2007; ARIENZO et al., 2009).

Ionic tolerance may be an indicator of environmental quality leading to rational applications for the maintenance of soil conditions suitable for a long-term cultivation and for the avoidance of any groundwater contamination (HARRIS; URIE, 1983; GRATAN; GRIEVE, 1992). However, a limitation to the above technological application is the lack of a specific device to provide instantaneous readings of the chemical quality of wastewater and, consequently, a better management in this particular source of soil alteration.

Electrolytic cells in the soil profile but close to the root system of crops may be an efficient tool in monitoring the natural recycling of ions. As an alternative to direct methods of analysis or to the use of tensiometer (GHIBERTO et al., 2009), the surface gamma-neutron gauges (REICHARDT;

TIMM, 2004) and the time domain reflectometry (LOPES et al., 2010), the electrolytic cells may estimate indirectly the leaching of hazardous substances, soil salinity, the electrical conductivity of soil solution, contents of potassium, nitrates, nitrites, and several heavy metals (YARON et al., 1996; SILVA et al., 2000).

Current experiment aims at the calibration of a manufactured electrolytic cell device for instantaneous readings at the correct point in the soil profile, sufficiently reliable for measuring the resistivity in the soil solution and not expensive for soil or environmental management.

Material and methods

The components consist of an electrolytic cell, a thermocouple, a vacuum system (Figure 1) and an electrical circuit performing a continuous current (Figure 2).

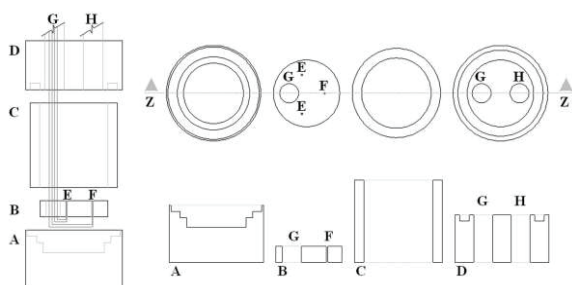


Figure 1. Diagram of the electrolytic cell indicating in the sectional plane Z – Z the cell base A, the electrode and thermocouple supporter B, the ceramic cylinder C, the upper face of the cell D, the electrodes E, the thermocouple F, the tubing system for the electrical circuits G, and the vacuum system H.

The electrolytic cells have a ceramic cylinder, 0.01 high and diameter 0.0175 m, featuring permeability to soil solution up to 0.080 MPa. Two opposite gold electrodes, diameter 0.005 m, were attached to the underside of the cylinder, 0.005 m from the center and close to the copper constantan thermocouple wire, optimizing the cell performance.

Terminals, thermocouple and display were connected by an electric circuit trespassing the upper side of the cylinder, whereas the vacuum system was connected by a polyethylene tube. A digital multimeter Minipa, model ET-2042, performed readings in voltage and temperature. The conditioning circuit was similar to Wheatstone bridge (EISBERG; LERNER, 1981; MIODUSKI, 1982; FIALHO, 2002) with the electrical resistance having an identical potential in the two circuit branches.

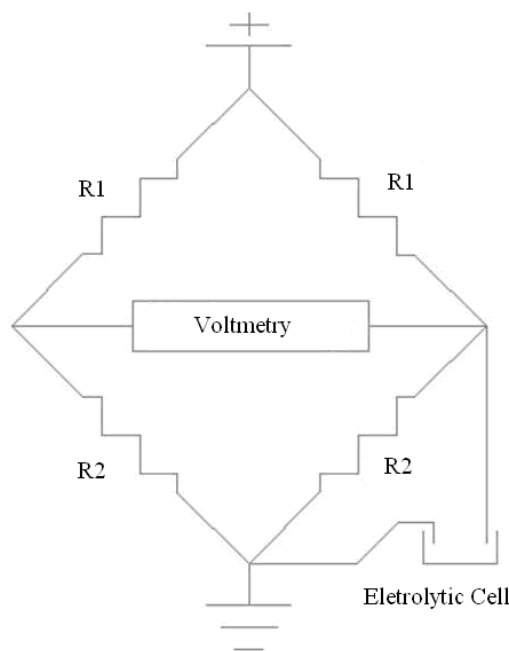


Figure 2. Diagram indicating the bridge and the electrolytic cell, in which R1 and R2 are circuit resistances.

The electrolytic cell was disposed as a by-pass in one of the resistors so that any redox reaction (ATKINS; PAULA, 2002) between electrodes and electrolyte inside the cell caused a difference in the electric potential which was indicated on the voltmeter display (EISBERG; LERNER, 1981; MIODUSKI, 1982; FIALHO, 2002). A 5 V tension in the bridge was the voltage which trespassed the resistors; the resistance in R1 in the conditioning circuit was 4.7 k Ω , while in R1 the 6.8, 15, 150 and 470 k Ω were tested to find the correct resistor rate for the present application. The calibration temperatures were 274, 281, 286, 291 and 298 K.

Three replicates of the device (C_1 , C_2 , C_3) were manufactured and compared to each other with F-ratio tests in which $F = (\text{difference } MS_i)/s^2$ for $F_{0.01}(2, 19)$ after linear analysis of regression (MEAD et al., 1993).

After the readings from standard solutions of potassium chloride at concentrations ranging between 10^{-4} and 10^{-1} mol L $^{-1}$ at 25°C, the voltage data sets versus the concentrations were individually fitted by linear regression procedure; similarly for the cassava wastewater (Table 1) for dilutions between 8.2×10^{-3} and 8.2×10^{-5} mol L $^{-1}$. Potassium chloride was chosen for the calibration due to its widespread occurrence in the cassava industrial wastewaters.

Table 1. Chemical composition in wastewater from cassava agro-industrial plants.

Total nitrogen	mg dm ⁻³	28.8
Organic carbon	mg dm ⁻³	74.0
Magnesium	mg dm ⁻³	11.27
Dissolved oxygen	mg dm ⁻³	4.0
Potassium	mg dm ⁻³	319.0
Calcium	mg dm ⁻³	9.69
Sodium	mg dm ⁻³	27.4
BOD	mg dm ⁻³	52.2
COD	mg dm ⁻³	140.6
pH		7.9
Electrical conductivity	dS m ⁻¹	0.049

Under the general law of Debye-Hückel, the relation between ion activity and electric potential, following Nernst's model, was employed to determine the coefficient of activity of K⁺ after appropriate corrections of the thermal effect and electrical current, according to the Equation (1)

$$E_{\text{cel}} = E_0 - \frac{RT}{nF} \ln a - C_f \quad (1)$$

where:

in which E_{cel} is the potential of electrolytic cell V;

E_0 is the standard potential of 4.85 V;

R is the gas constant 8.31447 J K⁻¹ mol⁻¹;

F is Faraday's constant, 96485.3 C mol⁻¹;

T is the temperature, K;

a is the ionic activity, a-dimensional;

C_f is the correction of the model.

$$C_f = \rho_0 + \rho_1 I + \rho_2 T \quad (2)$$

where:

ρ_0 , ρ_1 , ρ_2 are the parameters, I is the electric current in the electrolytic cell, A.

Results and discussion

There were no significant differences when the data sets from the three electrolytic cells were compared by the F-ratio test ($p > 0.01$), which suggested reproducibility in the manufacture of the present device (Figure 3). Under calibration conditions of the aqueous potassium chloride solution, identical and more sensitive response was found with 150 or 470 k Ω than with 6.8 or 15 k Ω in R2 when R1 had 4.7 k Ω (Figure 4).

After the better resistor choice of 4.7 k Ω for R1 and 150 k Ω for R2, the steady tension 4.85 V found in the empty cell became the standard potential. The overestimated potentials were found by Nernst's equation, corroborated by Skoog et al. (1997). Under thermal conditions between 273 and 373 K, the viscosity of aqueous solution was changed (ATKINS; PAULA, 2002; REICHARDT; TIMM,

2004) and Nernst's equation overestimated the potential, probably due to the characteristics of the continuous electric current (SKOOG et al., 1997; ATKINS; PAULA, 2002). Correction according to the electrical current and the temperature is necessary, and a linear trend for the electrical current (I) as well for the temperature (T) was found in which

$$C_f = 0.11847 + 3904.169 I + 0.0011 T \quad (3)$$

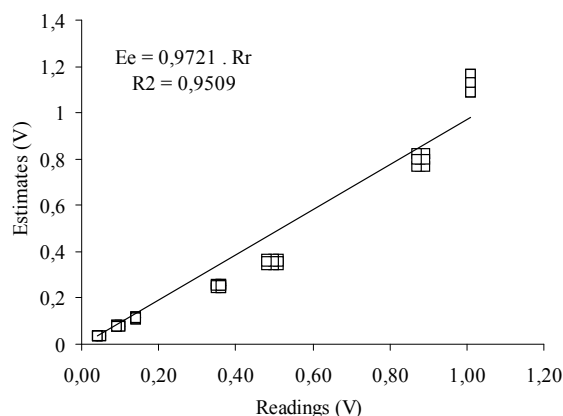


Figure 3. Readings of potential (R_r) versus estimates (E_e) from equation $V_L = \beta C^{1/2}$, in which V_L is the electrolytic potential from each cell; β is a coefficient; C is the concentration of the potassium chloride in the solution.

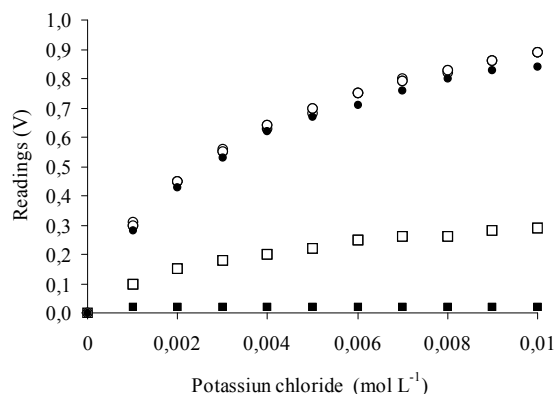


Figure 4. Electrical potential readings versus potassium chloride concentration for R_2 with 6.8 (■); 15 (□); 150 (●) and 470 k Ω (○).

After this correction, estimated potentials were provided by the following equation

$$E_{\text{cel}} = 4.73 + (1.10 \times 10^{-3} - 8.69 \ln a) T + 3.9 \times 10^3 I \quad (4)$$

where:

E_{cel} is the potential from the electrolytic cell, V;

a is the ionic activity by the general law of Debye-Hückel, making possible accurate measurements for wastewaters from cassava industries ($R^2 = 99.99\%$), as indicated in Figure 5.

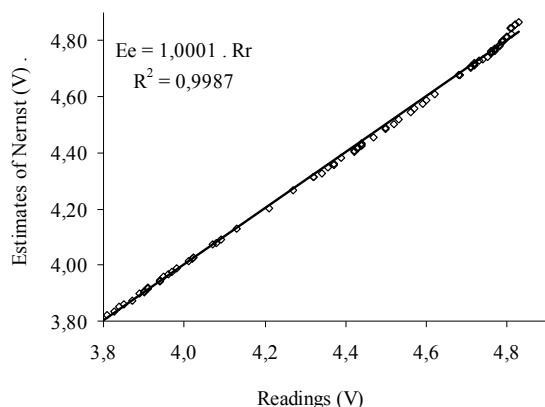


Figure 5. Reading potential (Rr) from electrolytic cells and estimates (Ee) from Nernst's model after the correction factor for potassium from diluted wastewater solutions.

Conclusion

Similar performance of electrolytic cells indicates reliability in manufacturing the device. Potassium from cassava wastewaters may be estimated with accuracy after appropriated calibration for electrical current and temperature.

References

- ARIENZO, M.; CHRISTEN, E. W.; QUAYLE, W.; KUMAR, A. A review of the fate of potassium in the soil-plant system after land application of wastewater. **Journal of Hazardous Materials**, v. 164, n. 2-3, p. 415-422, 2009.
- ATKINS, P.; PAULA, J. **Physical chemistry**. New York: Oxford University Press, 2002.
- EISBERG, R. M.; LERNER, L. S. **Physics, foundations and applications**. New York: McGraw-Hill, 1981.
- FIALHO, A. B. **Instrumentação industrial: conceitos, aplicações e análises**. São Paulo: Érica, 2002.
- GHIBERTO, P. J.; LIBARDI, P. L.; BRITO, A. S.; TRIVELIN, P. C. O. Leaching of nutrients from a sugarcane crop growing on an Ultisol in Brazil. **Agricultural Water Management**, v. 96, n. 10, p. 1443-1448, 2009.
- GRATTAN, S. R.; GRIEVE, C. M. Mineral element acquisition and growth response of plants grown in saline environments. **Agriculture, Ecosystems and Environment**, v. 38, n. 4, p. 275-300, 1992.
- HARRIS, A. R.; URIE, D. H. Changes in a sandy forest soil under northern hardwoods after 5 years of sewage effluent irrigation. **Soil Science Society of America Journal**, v. 47, n. 4, p. 800-805, 1983.
- HEIDARPOUR, M.; MOSTAFAZADEH-FARD, B.; KROUPAI, A.; MALEKIAN, R. The effects of treated wastewater on soil chemical properties using subsurface and surface irrigation methods. **Agricultural Water Management**, v. 90, n. 1-2, p. 87-94, 2007.
- JALALI, M.; MERIKHPOUR, H.; KALEDHONKAR, M. J.; VAN DER ZEE, S. E. A. T. M. Effects of wastewater irrigation on soil sodicity and nutrient leaching in calcareous soils. **Agricultural Water Management**, v. 95, n. 2, p. 143-153, 2008.
- JIMENEZ-CISNEROS, B. Wastewater reuse to increase soil productivity. **Water Science and Technology**, v. 32, n. 12, p. 173-178, 1995.
- KOLAHCHI, Z.; JALALI, M. Effect of water quality on the leaching of potassium from sandy soil. **Journal of Arid Environments**, v. 68, n. 4, p. 624-639, 2007.
- LEAL, R. M. P.; HERPIN, U.; FONSECA, A. F.; FIRME, L. P.; MONTES, C. R.; MELFI, A. J. Sodicity and salinity in a Brazilian Oxisol cultivated with sugarcane irrigated with wastewater. **Agricultural Water Management**, v. 96, n. 2, p. 307-316, 2009.
- LOPES, L. N.; SOUZA, C. F.; SANTORO, B. L. Utilização da TDR para monitoramento da solução de nitrato de potássio em latossolo vermelho-amarelo. **Engenharia Agrícola**, v. 30, n. 5, p. 932-947, 2010.
- MEAD, R.; CURNOW, R. N.; HASTED, A. M. **Statistical methods in agriculture and experimental biology**. 2nd ed. London: Chapman and Hall/CRC, 1993.
- MIODUSKI, A. L. **Elementos e técnicas modernas de medição analógica e digital**. Rio de Janeiro: Guanabara Dois, 1982.
- PEREIRA, B. F. F.; HE, Z. L.; STOFFELLA, P. J.; MELFI, A. J. Reclaimed wastewater: effects on citrus nutrition. **Agricultural Water Management**, v. 98, n. 12, p. 1828-1833, 2011.
- QADIR, M.; WICHELS, D.; RASCHID-SALLY, L.; MCCORNICK, P. G.; DRECHSEL, P.; BAHRI, A.; MINHAS, P. S. Challenges of wastewater irrigation in developing countries. **Agricultural Water Management**, v. 97, n. 4, p. 561-568, 2010.
- REICHARDT, K.; TIMM, L. C. **Solo, planta e atmosfera: conceitos, processos e aplicações**. Barueri: Manole, 2004.
- SILVA, E. F. F.; ANTI, G. R.; CARMELLO, Q. A. C.; DUARTE, S. N. Extratores de cápsulas porosas para o monitoramento da condutividade elétrica e do teor de potássio na solução de um solo. **Scientia Agrícola**, v. 57, n. 4, p. 785-789, 2000.
- SKOOG, D. A.; HOLLER, F. J.; NIEMAN, T. A. **Principles of Instrumental Analysis**. 5th ed. Fort Worth: Harcourt Brace College Publishers, 1997.
- TOZE, S. Reuse of effluent water – benefits and risks. **Agricultural Water Management**, v. 80, n. 1-3, p. 147-159, 2006.
- YARON, B.; CALVET, R.; PROST, R. **Soil pollution: processes and dynamics**. Berlin: Verlag Berlin Heidelberg, 1996.

Received on January 25, 2012.

Accepted on June 24, 2012.

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