ELECTROCHEMICAL ATTRIBUTES OF SOILS INFLUENCED BY SUGARCANE VINASSE

ATRIBUTOS ELETROQUÍMICOS DE SOLOS INFLUENCIADOS PELA VINHAÇA

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ABSTRACT: The electrochemistry at the surface of colloidal particles in soils is related to important physical and chemical phenomena, such as flocculation and dispersion of soil particles, cation-exchange-capacity, anion adsorption, pesticides and heavy metals adsorption. Sorption of organic compounds on the surface of soil components may cause important changes on their electrochemical attributes. The vinasse has been applied in soils, mainly in sugarcane crops, as organic fertilizer. Its effects on physical, chemical and biological attributes of soils are well documented; however, little is known about the effects on electrochemical attributes. This work aimed to evaluate the effects of sugarcane vinasse on soil pH and zeta potential of the clay fraction of two Latosols (Oxisols) and an Argisol (Ultisol). The pH of soils amended with vinasse was measured in water and 1M KCl solution (ratio soil:water 1:2.5), and estimated the ∆pH (pH 1M KCl – pH in water). The zeta potential (ζ) of the clay fraction was determined by electrophoretic mobility in 0,01M NaCl solution adjusted to different pH values (2, 3, 5, 6, 7, 9 and 11), and estimated the point of zero charge (PZC) (ζ = 0). The soil pH and net charge of soils were clearly influenced by vinasse. These changes may influence important chemical and physical phenomena in soils and also help future studies involving vinasse in soils.

KEYWORDS: Soil chemistry. Zeta potential. Soil pH

INTRODUCTION

Colloidal surface charge at the solid-liquid interface is one of the most important attributes of soils related to physical and chemical phenomena, mainly in tropical soils which have pH-dependent charges. WEBER et al. (2005) found that these variable charges represented more than 70% of the total charge in surface samples (0-20 cm) of Oxisols.

Many methods and definitions have been proposed to describe the electrochemistry at the surface of colloidal particles in soils (FONTES et al., 2001). For example, the net charge of the soil particles can be estimated by the difference between 1M KCl- and -water pH values, which is called ∆pH (ALLEONI; CAMARGO, 1994; SILVA et al., 1996), where the negative value indicates negative charge, positive value indicates positive charge, and ∆pH = 0 indicates a neutral condition or the point of zero charge (PZC).

Another way to assess the net surface charge of the soil particles is through the zeta potential (ζ) (TAN, 1993; ALKAN et al., 2005). In this case, ζ is defined as the electrical potential by the surface of the soil colloids bearing pH-dependent (TAN, 1993); it can be estimated by electrophoretic mobility of a soil colloidal suspension in an electric field (ZSE et al., 2003).

Electrochemical attributes are influenced by soil constituents such as phyllosilicate minerals, iron and aluminum oxides, and organic matter. The oxides contribute to increase the net positive charges and PZC in soils, whereas phyllosilicate minerals and organic matter increase net negative charges and reduce the PZC (GILLMAN, 1985; van RANST et al., 1998; ZHUANG; YU, 2002; ANDA et al., 2008). Highly-weathered tropical soils are dominated by 1:1 clay minerals, especially by the kaolinite, and by iron and aluminum oxides (SCHAEFER et al., 2008). Sorption of cations, anions and organic compounds on the surface of soil components may cause important changes on their electrochemical attributes (STOOP, 1980; LIMA et al., 2000; MARCHI et al., 2006). It was hypothesized that dissolved organic compounds present in the vinasse (DOELSCH et al., 2009) may change electrochemical conditions at these surfaces.

The vinasse is the main by-product of the ethanol industry; this activity is in large expansion in Brazil (OLIVEIRA et al., 2005; LEE; BRESSAN, 2006; SORATTO et al., 2007; GOLDEMBERG et al., 2008). In the past, vinasse was dumped into streams, rivers and lakes, increasing pollution and degradation in the environment (GÜN KEL et al.; 2007; MARTINELLI; FILLOSO, 2008). This is now prohibited. One of the alternatives for producers to get rid of vinasse is to add it to soils as
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an organic fertilizer, mainly in the sugarcane crops (FREIRE; CORTEZ, 2000).

The vinasse has high biochemical oxygen demand, low pH, high organic matter (organic acids and sugars), and high amount of potassium (FREIRE; CORTEZ, 2000; DOELSCH et al., 2009). Although the effects of vinasse on soil pH is well known (LEAL et al., 1983; MATTIAZZO; GLÓRIA, 1987; DOELSCH et al., 2009), there are still some issues, such as the effect of vinasse on electrochemical attributes of the soil particles such as zeta potential, to be elucidated. Changes on surface charges of soil colloids are basic to understand flocculation and dispersion of soil particles, cation-exchange capacity, anion adsorption, pesticides and heavy metals adsorption. Thus, the objective of this work was to evaluate the changes on soil pH (in water and 1 M KCl solution), ΔpH, and zeta potential of the clay fraction from surface samples of a Latossolo Vermelho Distroférico (LVdf), Latossolo Vermelho-Amarelo Distrófico (LVAd) and Argissolo Vermelho-Amarelo Distrófico (PVAd), two Oxisols and one Ultisol respectively (U.S. Taxonomy), as affected by the use of the vinasse.

MATERIAL AND METHODS

Topsoil samples (0-10 cm) of a Latossolo Vermelho Distroférico (LVdf), Latossolo Vermelho-Amarelo Distrófico (LVAd) and Argissolo Vermelho-Amarelo Distrófico (PVAd), according to Brazilian System of Soil Classification (EMBRAPA, 2006), two Oxisols and one Ultisol respectively (U.S. Taxonomy), were selected for this study. Selected attributes of the soil samples are reported in Table 1.

Table 1. Selected attributes of topsoil samples (0-10 cm) of Latossolo Vermelho Distroférico (LVdf), Latossolo Vermelho-Amarelo Distrófico (LVAd) and Argissolo Vermelho-Amarelo Distrófico (PVAd).

<table>
<thead>
<tr>
<th>Attributes</th>
<th>LVdf</th>
<th>LVAd</th>
<th>PVAd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay (g kg⁻¹)</td>
<td>714</td>
<td>615</td>
<td>445</td>
</tr>
<tr>
<td>Silt (g kg⁻¹)</td>
<td>112</td>
<td>45</td>
<td>197</td>
</tr>
<tr>
<td>Sand (g kg⁻¹)</td>
<td>174</td>
<td>340</td>
<td>358</td>
</tr>
<tr>
<td>SiO₂ (g kg⁻¹)</td>
<td>167</td>
<td>135</td>
<td>177</td>
</tr>
<tr>
<td>Al₂O₃ (g kg⁻¹)</td>
<td>257</td>
<td>90</td>
<td>194</td>
</tr>
<tr>
<td>Fe₂O₃ (g kg⁻¹)</td>
<td>219</td>
<td>90</td>
<td>71</td>
</tr>
<tr>
<td>K</td>
<td>1.11</td>
<td>2.53</td>
<td>1.54</td>
</tr>
<tr>
<td>pH</td>
<td>6.0</td>
<td>5.8</td>
<td>5.9</td>
</tr>
<tr>
<td>P (mg dm⁻³)</td>
<td>3.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>K⁺ (mg dm⁻³)</td>
<td>73</td>
<td>28</td>
<td>33</td>
</tr>
<tr>
<td>Ca²⁺ (cmol_c dm⁻³)</td>
<td>2.0</td>
<td>2.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Mg²⁺ (cmol_c dm⁻³)</td>
<td>0.5</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Al³⁺ (cmol_c dm⁻³)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>H⁺Al (cmol_c dm⁻³)</td>
<td>3.9</td>
<td>4.8</td>
<td>2.9</td>
</tr>
<tr>
<td>SB (cmol_c dm⁻³)</td>
<td>2.7</td>
<td>3.3</td>
<td>2.8</td>
</tr>
<tr>
<td>CEC⁺⁺⁺₃⁺ (cmol_c dm⁻³)</td>
<td>2.9</td>
<td>3.5</td>
<td>3.0</td>
</tr>
<tr>
<td>CEC⁺⁺⁺⁺ (cmol_c dm⁻³)</td>
<td>6.6</td>
<td>8.1</td>
<td>5.7</td>
</tr>
<tr>
<td>V (%)</td>
<td>41</td>
<td>41</td>
<td>49.1</td>
</tr>
<tr>
<td>m (%)</td>
<td>7.0</td>
<td>5.7</td>
<td>7.0</td>
</tr>
<tr>
<td>OM (g kg⁻¹)</td>
<td>30</td>
<td>31</td>
<td>22</td>
</tr>
</tbody>
</table>

After ultrasonic dispersion of soil suspension in water (10 g of soil in 200 mL of distilled water) for 16 minutes (336 J mL⁻¹); ² Total oxides in the clay fraction; Ki: (SiO₂/Al₂O₃) molecular ratios; pH measured in 1:2.5 soil:water ratio; SB: sum of bases (Ca²⁺, Mg²⁺ and K⁺); ³ Cation exchange capacity in natural pH of soil; ⁴ Cation exchange capacity in pH 7.0; V: saturation by bases on cation exchange capacity; m: saturation by Al³⁺ on cation exchange capacity in natural pH of soil; OM: organic matter. All attributes were measured according to EMBRAPA (1997).

The samples were air-dried for 72 hours, ground and sieved to obtain 1-2 mm aggregate size fraction. An equivalent to 200 g oven-dried (105°C) aliquot was placed into 250-mL plastic bottles; the bulk density was 1.00 g cm⁻³ ± 0.04. Then, different doses of vinasse, 0 (control) and the equivalent to 150 and 300 m³ ha⁻¹ were applied. The highest dose was enough to saturate the micropores of the sample, which were approximately 0.30 cm³ cm⁻³ in all the soil samples. The samples were incubated during 1, 30 and 60 days, keeping the moisture at the field capacity with distilled water on weight-
basis. After incubation, the samples were air-dried and stored for further pH measurements. The vinasse was acidic (pH = 3.5), with potassium content equal to 2.5 g L\(^{-1}\), solid residue (9.6 g L\(^{-1}\)), total organic carbon (9.0 g L\(^{-1}\)), and electrical conductivity (7.5 dS m\(^{-1}\)).

For pH determinations, 6 g of soil were placed into 25-mL glass bottles containing 15 mL of distilled water or 1 M KCl solution (soil: solution ratio = 1:2.5). The samples were shaken for 30 minutes in a horizontal shaker at 130 rpm at room temperature (22º C ±2). After shaking, the samples rested for 30 minutes to reach the equilibrium condition until the pH determinations. All analyses were made in triplicate. The ΔpH was obtained by the difference between pH in KCl and pH in water.

For clay extraction, approximately 50 g of the soil samples were placed into 250-mL glass bottles containing 200 mL of distilled water, and sonicated at 70 W for 16 minutes to complete soil dispersion. The sonication time was selected based on the plateau (maximum clay content) from dispersion curves of the soils previously obtained (data not showed) according to RAINE e SO (1993, 1994). The equipment used was a probe type Misonix, inserted to a depth of 25 mm into the suspension. After the ultrasonic dispersion, the suspension (clay plus silt) was sieved to remove sand fraction and transferred to measuring cylinders. The final volume was adjusted to 1 L with distilled water. The cylinders were shaken in order to homogenize the suspension. After adequate settling times (based on Stokes’ law), the clay fraction was extracted.

The clay fraction (0.1 g) was placed in 25-mL glass bottles containing 10 mL of vinasse (soil suspension ratio = 1:100) and shaken for 4 hours in a horizontal shaker at 130 rpm and room temperature (22º C ±2). After shaking, the samples were centrifuged for 10 minutes at 500 G and the pH and the electrical conductivity of the supernatant were measured. The supernatant was discarded and the clay fraction was lyophilized and stored for zeta potential determinations.

A clay suspension was prepared with 0.1 g in 40 mL of NaCl 0.01 M. Triplicate 4-mL aliquots were transferred to 50-mL beaker containing 40 mL of NaCl 0.01 M at different pH values (2, 3, 5, 6, 7, 9 and 11.0 ±0.2), previously adjusted with HCl or NaOH 0.01 M. These suspensions were placed into a Zeta Meter electrophoretic cell (Zeta Meter System 3.0+) for ζ determinations. The voltage was set up to give a tracking of soil particles of ~ 5 s. A total of 10 to 20 particles were counted for each procedure. The ζ values obtained were plotted against the pH values and adjusted to a polynomial cubic model. The point of zero charge (PZC) was estimated by the model when the ζ was equal to 0.

For pH results, the data were submitted to variance analysis (F Test) and the averages compared based on standard deviation. For zeta potential results, the significance of the fit of the polynomial cubic model adjusted was evaluated by variance analysis (F Test) and R\(^2\) value.

**RESULTS AND DISCUSSION**

With 1 day incubation time, it was observed that the vinasse doses applied reduced the pH in water, compared to control, except in the PVAd sample (Figure 1). An initial decrease in pH in water was also observed in the soils that received the equivalent to 500 m\(^3\) ha\(^{-1}\) of vinasse (MATTIAZZO; GLÓRIA, 1987). The acidity of vinasse (pH = 3.5) initially contributes to increase H\(^+\) in soil solution and, consequently, decrease the pH. For pH in KCl, in all soils, the initial reduction was not observed (Figure 1).

In all soils, as the incubation time increased the pH in water and 1-M KCl solution increased significantly with the vinasse doses applied (Figure 1), overcoming the pH of the control sample. Due to the high biochemical oxygen demand, vinasse causes a temporally reducing environment. In this condition, ions H\(^+\) become the final electron acceptors. As the ions H\(^+\) are reduced the pH increases (LEAL et al., 1983; MATTIAZZO; GLÓRIA, 1987; DOELSCH et al., 2009). DOELSCH et al. (2009) observed that the increase in pH was followed by a significant decrease in oxidation potential (Eh), indicating a more reducing environment. However, this process occurs only with microbial activity, as demonstrated by MATTIAZO; GLÓRIA (1987). These authors observed that in previously sterilized soils the vinasse did not affect pH. The increase in pH observed by DOELSCH et al.(2009) was also related with the increase in the microbial activity measured by CO\(_2\) evolution.

The highest dose of vinasse accounted for the highest increase in pH. This may be related to the higher amount of organic compounds from vinasse incorporated into the soil samples, favoring the process described above. There was no significant difference between pH values at 30 and 60 days, for the same vinasse dose applied. The pH may drop after 60 days reaching the value of the control sample again, when the decomposition of all organic compounds from vinasse has finished. In aerobic conditions, it was observed that only 12.8 %

of the initial dissolved organic carbon from vinasse remained in the soil after 28 days (DOELSCH et al., 2009).

Regarding the ΔpH (pH in KCl – pH in H₂O) as an estimate of the net surface charge of the soil particles (Figure 2), the LVdf and LVAd became positive at day 1. At 30 and 60 days, the LVdf remained neutral (ΔpH = 0) in both vinasse doses. At 30 days of incubation, the LVAd showed a slight negative charge, becoming neutral at 60 days for the lowest applied vinasse dose and with a negative value about the same as the control, at the highest dose of applied vinasse. The PVAd remained negative in all conditions. The neutral conditions reached at the clay particles of LVdf and LVAd may account for higher flocculation of soil particles (TAN, 1993).

**Figure 1.** Effect of vinasse and incubation time on pH in water and 1M KCl of topsoil samples (0-10 cm) from a Latossolo Vermelho Distroférrico (LVdf), Latossolo Vermelho-Amarelo Distrófico (LVAd) and Argissolo Vermelho-Amarelo Distrófico (PVAd). Error bars indicate the standard deviation (n=3). * Significant (p<0.05 – F Test). ns: no significant.
As expected, the clay fraction had a pH-dependent surface charge as it can be seen from the comparison of zeta potential with the pH values (Figure 3). The data were well fitted to polynomial cubic model, with R^2 ranging from 0.94 to 0.98 (Table 2).

Figure 2. Effect of vinasse and incubation time on ΔpH (pH 1M KCl – pH in water) of topsoil samples (0-10 cm) from a Latossolo Vermelho Distroférrico (LVdf), Latossolo Vermelho-Amarelo Distrófico (LVAd) and Argissolo Vermelho-Amarelo Distrófico (PVAd). Error bars indicate the standard deviation (n=3).

Figure 3. Effect of vinasse on zeta potential of the clay fractions of topsoil samples (0-10 cm) of a Latossolo Vermelho Distroférrico (LVdf), Latossolo Vermelho-Amarelo Distrófico (LVAd) and Argissolo Vermelho-Amarelo Distrófico (PVAd). Error bars indicate the standard deviation (n=3).
Table 2. Polynomial cubic equations adjusted to zeta potential (ζ) as a function of pH of the clay fraction of Latossolo Vermelho Distroférico (LVdf), Latossolo Vermelho-Amarelo Distrófico (LVAd) and Argissolo Vermelho-Amarelo Distrófico (PVAd) under the influence of vinasse.

<table>
<thead>
<tr>
<th>Clay Fraction</th>
<th>Control ζ (±std)</th>
<th>Vinasse ζ (±std)</th>
<th>Equation</th>
<th>$R^2$</th>
<th>PZC$^{1/}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVdf</td>
<td>181.22 -75.78pH + 9.88pH$^2$ -0.43pH$^3$</td>
<td>115.19 - 52.15pH + 7.24pH$^2$ - 0.33pH$^3$</td>
<td>0.97</td>
<td>4.6 (± 0.05)</td>
<td></td>
</tr>
<tr>
<td>LVAd</td>
<td>160.57 - 71.95pH + 9.64pH$^2$ - 0.42pH$^3$</td>
<td>65.13 - 31.98pH + 4.57pH$^2$ - 0.21pH$^3$</td>
<td>0.97</td>
<td>3.2 (± 0.00)</td>
<td></td>
</tr>
<tr>
<td>PVAd</td>
<td>122.38 - 54.67pH + 7.06pH$^2$ - 0.30pH$^3$</td>
<td>89.89 - 39.20pH + 5.12pH$^2$ - 0.22pH$^3$</td>
<td>0.94</td>
<td>3.9 (± 0.02)</td>
<td></td>
</tr>
</tbody>
</table>

$^{1/}$ Obtained when $\zeta = 0$. Values in parentheses indicate the standard deviation (n = 3).

As the pH increased the zeta potential reduced, indicating that the surface of clay fraction became gradually more negative. LVdf clay had a surface potential of +20 mV at pH ~ 3.5 which decreased to -18 mV at pH near to 11.0. The PZC was 4.6. LVAd clay had a less positive zeta potential, at pH 3.5 (+ 9 mV), reaching the PZC at 4.1, becoming negatively charged (-21 mV at pH near to 11.0). PVAd clay showed the lowest zeta potential at pH 3.5 (+ 5.6 mV) reaching the PZC at pH 3.9. There were no differences for zeta potential among all the clay fractions for pH between 5.0 and 9.0.

These results support, in part, those results found by GIAVENO et al. (2008) that evaluated the zeta potential of the clay fraction of Oxisols from two different sites (site A – native cerrado and site B – vegetation represented by grass). According to those authors, clay A had the zeta potential ranging from + 8 mV (pH 2.5) to -30 mV at pH near to 7.0, reaching the PZC at pH 3.9. Clay B had a more positive charge at pH 2.5 (+ 18 mV). The PZC was reached at pH 5.3; after that it became gradually more negative, reaching -25 mV at pH near 7.0. The higher negative charge and the lowest PZC of the clay A were related to its higher content of organic matter.

In summary, the negative charge decreases as following: PVAd>LVAd>LVdf. For the PZC, the inverse trend was observed: LVdf>LVAd>PVAd. These results are related to the higher content of Fe oxides of Latosols (van RANST et al., 1998; ANDA et al., 2008), which contribute to increase the positive net charge and PZC of soils (Table 1). The color of the soils is reflecting such behavior.

When the clay fraction was treated with vinasse, the zeta potential was close to 0 (Figure 3), indicating that the soil charges were partially neutralized. It was also observed a slightly reduction in the PZC from 4.6 to 4.4 in the LVdf clay (Table 2). In the LVAd clay, the PZC was reduced from 4.1 to 3.2 and in PVAd clay a slight increase in the PZC from 3.9 to 4.1 was observed.

The results indicate that the periodical vinasse application in soils as organic fertilizer, may affect the pH and the surface charges of the soil particles; consequently, it may influence important phenomena such as soil dispersion and flocculation, erosion susceptibility, cation and anion exchange capacity, and metal and pesticide sorption. These aspects should be considered in terms of vinasse doses and frequency of application aiming to reach the environmental sustainability of ethanol exploration.

CONCLUSIONS

The soil pH and net charge of soils were clearly influenced by vinasse. Taking into account the known inter-relationships of these attributes and soil behavior, doses and application frequency of vinasse should be recommended and monitored considering the environmental sustainability of ethanol exploration.

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Argissolo. Foi determinado o pH em água e em solução KCl 1M (relação solo:água 1:2,5) e estimado o ΔpH (pH em KCl 1M – pH em água). Na fração argila foi determinado o potencial zeta (ζ) por mobilidade eletroforética em solução de NaCl 0,01M com diferentes valores de pH (2, 3, 5, 6, 7, 9 e 11) e estimado o ponto de carga zero (PCZ) (ζ = 0). O pH do solo e as cargas superficiais foram claramente influenciadas pela vinhaça. Essas mudanças podem influenciar importantes fenômenos físico-químicos do solo, bem como, servir de base para estudos futuros envolvendo vinhaça em solos.

PALAVRAS-CHAVE: Química do solo. Potencial zeta. pH do solo

REFERENCES


