Comparison of Methods for Organic Matter Removal Applied in Brazilian Ferralsols

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RESUMO – Latossolos podem apresentar dispersão deficiente na análise granulométrica, devido à presença de microagregados de alta estabilidade, contribuindo para superestimar a fração silte. O objetivo desse estudo foi avaliar qualitativamente os métodos do hipoclorito de sódio (NaClO) e peróxido de hidrogênio (H_2O_2) para remoção da matéria orgânica do solo (MOS) em horizontes A e B de cinco perfis de Latossolos de várias regiões do Brasil. O método do NaClO foi mais rápido e prático, porém mostrou interações com a fração mineral, haja vista o padrão de dispersão de amostras do horizonte A. As interações entre a MOS e os óxidos parecem regular o efeito dispersivo do NaClO. Já o H_2O_2 foi considerado inapropriado para laboratórios de análises de rotina, devido, principalmente, ao longo tempo necessário para completar a reação. Efeitos sobre a fração mineral foram deduzidos pela dispersão da fração mais fina e alterações em minerais no solo. Assim, a aplicabilidade dos dois métodos aos Latossolos requer adaptações e, portanto, estudos mais detalhados.

Palavras - chave: agentes cimentantes, pseudosilte, análise granulométrica.

Introduction

Ferralsols cover about 1/3 of Brazilian territory and represent the soil with the most intensive agricultural usage in the country [1]. Thus, knowledge of their properties is important for adequate management and land capability evaluation. Some Ferralsols show contradictory results in granulometric analysis, mainly due to incomplete clay dispersion related to presence of high-stability micro aggregates [2]. Cementing agents such as iron and aluminum oxides, carbonates, and organic matter (OM) are the main responsible for formation and maintenance of these aggregates [3].

Persistence of micro aggregates, after conventional dispersion treatments, results in an overestimation of silt and sand fractions. To minimize this negative effect, methods to remove cementing agents have been proposed [2; 4], but without conclusive results for high-weathered tropical soils.

This study aimed to compare and to evaluate qualitatively methods using sodium hypochlorite and hydrogen peroxide for removing soil OM of some Brazilian Ferralsols and their effect on clay dispersing.

Material and Methods

A. Characteristics of Soil Samples

Soils used in this study were classified as Ferralsols by FAO/ISRIC/ISSS [5] and Latossolos by EMBRAPA [6]. Table 1 presents data of organic carbon (C_{org}) content, pH and granulometrical composition of A and B horizons of the five studied soils. Soil texture ranged from sandy loam to clayey and C_{org} content from 8 to 40 g kg^{-1}.

B. Treatments

Two wet oxidative treatments were tested:
- Sodium hypochlorite, NaClO (adapted from Anderson [7]): 20 ml of NaClO 5-6 % available chlorine at pH 9.5 (freshly adjusted with concentrated HCl) were added to 10 g soil sample in a 50 mL-plastic centrifuge tube. After homogenization, samples were taken to a hot water bath (75 to 80 ℃), and let to react for 15 minutes. Samples were centrifuged for 10 min at 2500 rpm and the supernatant saved for further analysis. Treatment was repeated four times. Another trial using diluted NaClO (10% v/v) was carried out to evaluate its dispersing effect.
- Hydrogen peroxide, H_2O_2 (adapted from EMBRAPA [8]): 25 mL of distilled water and 3-5 mL of H_2O_2 30 % (v/v) were added to 25 g soil sample in a 100 mL-glass flask. After homogenization, the flask was covered with a watch glass and the suspension left to react for 12 h at room temperature. H_2O_2 was added twice a day until no more soil sample frothing was observed. Samples were taken to a hot plate (50-60 °C) to reduce water content, when additional 10 mL of H_2O_2 were added to remove residual OM. Then, the samples were poured into a funnel-filter apparatus and washed with distilled water several times. Drying was carried out at room temperature.

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Results and Discussion

A. Sodium Hypochlorite

The method first proposed by Anderson [7] suggested a centrifugation time of 5 to 10 min at 800 rpm. This step was modified to 10 min at 2500 rpm, to avoid loss of fine-size soil particles in clayey samples.

Soil frothing was expressive in higher OM content samples (A horizons from P3 and P5) in the first extraction, and it resulted in loss of soil material. Two steps are suggested to avoid the soil loss: using a higher capacity container, which size is often controlled by the centrifuge capacity; or carrying out the first extraction at room temperature and using a soil to NaClO ratio of less then 1:2, making the method time consuming.

The color of the supernatant obtained in the initial extraction was yellow to strong-yellow as the sample OM content increased. In following extractions the supernatant color became clearer, similar to the reactant (yellowish), indicating that a great part of the OM had been already removed (Figure 01).

The dispersing effect of NaClO was evaluated by Omueti [9], in soils of Nigeria. In that case, NaClO was effective only for sandy to sand loamy textured soils; and dispersion was not efficient in fine textured soils. In this study, soil dispersal was observed in all textural classes' samples; however, OM content seems to play an important role on this phenomenon, since soil dispersal was prominent in A horizons (Figure 02).

After NaClO extraction of OM, Anderson [7] recommends the use of a sodium carbonate-sodium bicarbonate solution (pH 9.5), for final reduction of salt content and Na saturation. Unfortunately, this step was inadequate for the Brazilian Ferralsols, since soil dispersal occurred to a great extend and centrifugation at 2500 rpm was unsuccessful to separate the solid phase. Thus, if the supernatant was discarded, the loss of soil mineral particles would result in underestimation of clay content in the granulometric analysis. To avoid this undesirable effect it is necessary to verify in which cases further treatments for Na saturation is worth and to decide on another reactant to carry out this step.

It is also necessary to evaluate the effects of NaClO on mineral constituents, since it extracts microelements associated with OM [10]. When released, these organically bound metals may precipitate as (hydr)oxides both in inorganic and organic components, due to the high solution pH (9.5) [4]. In Ferralsols these oxides, especially Fe ones, play a major role on soil OM stabilization [11], what may reduce the effectiveness of NaClO treatment. In the same way, minerals may go through heat-induced changes, as verified by Lavkulich & Wiens [12], going into more crystalline forms. To avoid this effect Kaiser et al. [13] proposed use of NaClO at room temperature, what is time consuming, since extended contact is required.

In addition to the above notes on efficiency of NaClO method as an OM extraction treatment, there is an aspect of great importance for healthcare: the formation of haloorganic compounds during OM oxidation, such as trihalomethanes and haloacetic acids [14], known by their high carcinogenic potential.

B. Hydrogen Peroxide

EMBRAPA [8] recommends the usage of hydrogen peroxide as pre-treatment for OM removal in two cases: 1) prior to granulometric analysis, for soils with more than 50 g kg^{-1} of OM; and 2) prior to mineralogical analysis, mainly on soils with 2:1 clay minerals, by means of X-ray difratometry, for samples containing more than 10 g kg^{-1} of organic C. The setback of this methodology was the extended contact time required for the reaction to occur. At routine laboratories, such time-consuming method is not preferred and may be rejected.

It is also important to note that the method as described by EMBRAPA [8] lacks some procedure details. Among those, four were of most importance: 1) relation between soil sample and container size; 2) amount of water and reactant to be added; 3) use of heating devices; and 4) specification of paper filter for sample washing.

Soil frothing was very expressive during OM oxidation by H_2O_2 of the samples, and it lasted until no additional organic compounds could be oxidized. In the highest OM content samples (A horizon from P3 and P5) soil frothing was substantial and resulted in soil loss, requiring a larger size container. The amount of water added to suspension interfered in the procedure as well, and it was necessary to evaporate excess in a hot plate after ten additions of H_2O_2. Some authors recommend usage of high temperatures (> 70 ºC) to shorten time to oxidize OM [15]. However, high temperature accelerates H_2O_2 decomposition and promotes changes on soil minerals.

Attempting to avoid excessive soil frothing, first additions of H_2O_2 were made on the following bases: 3 mL for the highest and 5 mL for lowest OM content samples. When frothing intensity was similar among all samples, H_2O_2 additions were of 5 mL till completion. As soon as frothing stopped, samples were taken to a hot plate to dry. However, loss of soil was also observed in this step - reduced metals and mineral surfaces catalyze excess H_2O_2 decomposition into H_2O and O_2, a new source of frothing.

Sample washing step must also be reviewed, since qualitative filters were not suitable for clayey soils. In this case, an expressive soil loss occurred due to large pores size. On the other hand, quantitative filters retained soil particles efficiently, but increased time needed and also resulted in loss of material due to the strong attachment of soil to paper fibers (Figure 3a). Figure 3b shows another setback of using quantitative paper filter: after the sample was poured into the funnel-filter apparatus, the liquid phase showed an upward movement by capillarity, carrying fine-size particles. When the suspension reached the paper filter border, touching the funnel wall, it was noted a downward movement outside the filter, with soil loss.

Along these method issues, there are mineral-altering processes that may hold back H_2O_2 usage according to soil

clay mineralogy. Such as, organic ligand promotes dissolution of Fe oxides and may be one of most importance changes, since a variety of water-soluble compounds is yielded, such as oxalate [4]. Reductive dissolution of Fe^{III} to Fe^{II} may also act [16], especially at low pH, as found during H_2O_2 extraction. This may explain why some soil samples had greatest amount of fine-size particles in suspension after H_2O_2 treatment (Figure 3c). Further induced mineral changes are pointed out [4]: transformation of hydrated amorphous Al compounds into gibbsite; heat-induced transformation of Fe and Al oxides into more crystalline forms; and, exfoliation and/or destruction of phyllosilicates, as it seem to have happened in P3 samples (Figure 3d).

C. Final Considerations

Both pretreatment methods for soil OM removal showed negative aspects that holdback their usage in routine soil analysis laboratories. Interaction of soil OM and Fe/Al (hydr)oxides seems to be controlling most discussed issues. Results obtained in this study are in agreement with those of Donagemma et al. [2], who concluded that poorly-crystallized Fe and Al oxides removal might be more effective in reducing factors affecting soil dispersal than OM removal.

Conclusions

The efficiency of NaClO and H_2O_2 methods for OM removal in high-weathered oxidic soils still is under discussion. In the same way, the knowledge about its effects on selected soil minerals is incomplete. At the moment, use of either reactant prior to granulometric analysis of Brazilian Ferralsols depends on method adjustments. Thus, more research is needed to answer the following questions:

1. How OM-oxides interactions can affect OM removal efficiency and the dissolution of Fe and Al oxides?
2. What is the Fe and Al oxide content above which OM removal becomes unfruitful? Can the amount of poorly and well-crystallized constituents affect this value?
3. How changes in temperature and time of exposure can affect OM removal and mineral alterations?
4. Can exfoliation and/or destruction of phyllosilicates by H_2O_2 affect granulometric analysis?
5. Is there another potential oxidizing reactant that may minimize the setbacks found in NaClO and H_2O_2-based methods for high-weathered oxidic soils?
6. How harmful are haloorganic compounds formed during OM oxidation by NaClO? If the carcinogenic potential is great, it should be avoided, and if mild, how can personnel exposure be reduced or eliminated?

Acknowledgements

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Table 01. Granulometrical composition, pH and organic carbon content of A and B horizons from five Brazilian Ferralsols[1].

Horizon	pH water	Sand	Silt	Clay	Organic C
		------------------------------------ g kg^{-1} ----------------------------------			
Profile 1 (P1) – LATOSSOLO VERMELHO-AMARELO, Piracicaba, São Paulo. [2]					
A	5.5	750	92	158	8
B	5.5	730	78	192	4
Profile 2 (P2) – LATOSSOLO VERMELHO, São Carlos, São Paulo. [3]					
A	5.1	689	99	212	11
B	4.8	667	39	294	8
Profile 3 (P3) – LATOSSOLO VERMELHO-AMARELO, Nova Friburgo, Rio de Janeiro. [4]					
A	5.2	350	160	490	30
B	4.7	350	100	550	10
Profile 4 (P4) – LATOSSOLO VERMELHO, Patos de Minas, Minas Gerais. [5]					
A	5.2	80	139	702	26
B	4.9	66	89	780	24
Profile 5 (P5) – LATOSSOLO VERMELHO, Sete Lagoas, Minas Gerais. [6]					
A	5.7	110	130	750	40
B	5.2	90	50	870	15

[1] Soils are classified according to Brazilian Soil Classification System [6].
[2] Vidal-Torrado et al. [17].
[3] Calderano Filho et al. [18].
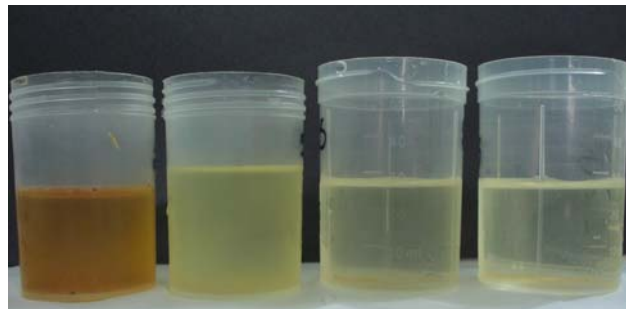[4] EMBRAPA [19].
[5] EMBRAPA [20].
[6] Viana [21].
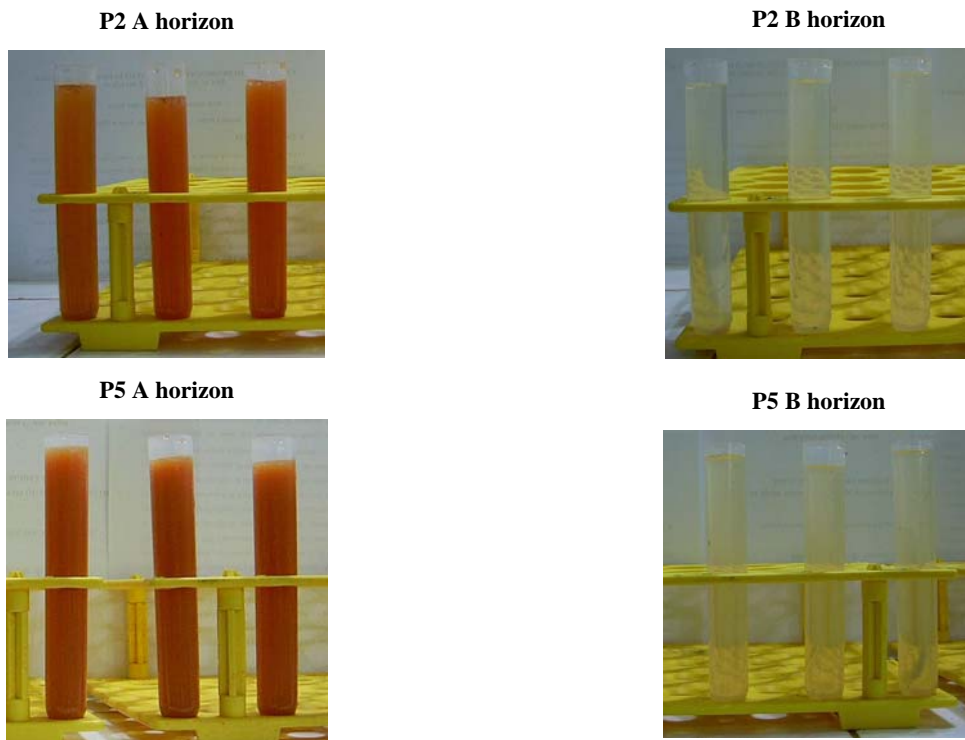
P3 A horizon   **P5 A horizon**

Figure 01. Extracts obtained from sequential treatments of soil samples for organic matter removal with sodium hypochlorite (NaClO) pH 9.5 (adapted from Anderson [7]). Seropédica, RJ, 2009.

Note: From left to right, first to last extraction.

P2 A horizon

P2 B horizon

P5 A horizon

P5 B horizon

Figure 02. Supernatant obtained from treatments of soil samples for soil dispersal and organic matter removal with sodium hypochlorite (NaClO) 10 % (v/v) pH 9.5 (adapted from Anderson [7]). Seropédica, RJ, 2009.

a)

b)

c)

d)
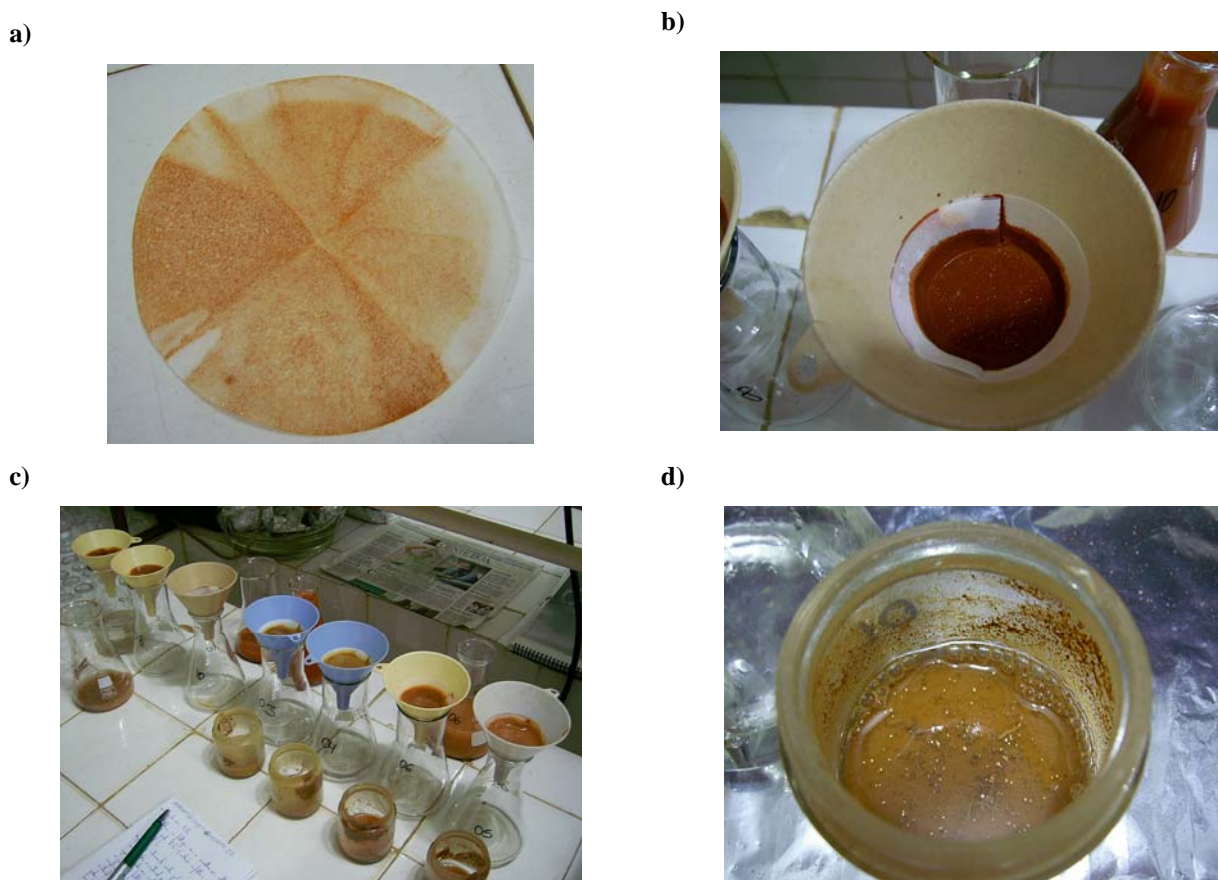
Figure 3. Quantitative paper filter impregnated by fine-size soil particles after sample washing (a); funnel-filter apparatus with sample showing upward movement by capillarity and consequent loss of soil material (b); sample washing set: in the back, samples containing a great amount of particles in suspension (c); glass container used for sample treatment: small shinny spots on sample surface (P3 Hz A e B) are micas altered by H_2O_2 30% (v/v). Seropédica, RJ, 2009.