

# Phosphorus Collectors from Filter Paper and Synthetic Cloth Coated with Iron or Aluminium Oxide to Provide Phosphorus by Diffusion in Soils

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## ABSTRACT

*Phosphorus collectors made from filter paper and synthetic cloth, were tested to evaluate their feasibility of determining the need for phosphate application. The collectors were coated with two types of oxides, iron oxide and aluminium oxide. The capacity of the collectors was tested by placing them in a 2 mL of solution containing phosphorus ( $PO_4^{3-}$ ) in the concentration of 0.0, 1.00, 3.00, 5.00, 7.00, 9.00 and 11.00  $mg \cdot mL^{-1}$ , respectively, after which they were placed in contact with four types of soil (LBa, LRd, LEd and Ca) and incubated for 0.0 and 24 h. In this test the soils were kept at a humidity equivalent to 150 mmHg suction. The amount of phosphorus extracted from the solutions was tested at intervals between 0,0 and 11.0  $mg$  of phosphorus/mL. Results indicated that collectors were most efficient in Dystrophic Dark-Red Latosol (LEd) and less efficient in "Bruno álico" Latosol (LBa) and Cambisol (Ca). Synthetic cloth was the support yielding the best performance, whereas iron oxide lining was the most adequate lining material. Phosphorus collection increased with time of incubation.*

**Key words:** phosphorus, phosphorus availability, phosphorus diffusion, phosphorus extraction.

## INTRODUCTION

Many methods have been used to determine the soil's capacity in providing phosphorus and other nutrients to plants. One of these methods is the extraction method using dilute acids. Another method which shows a better performance is the anion-exchanging resin (Raij & Quaggio, 1981). The latter method is somewhat better than that mentioned above (Anghinoni & Volkweiss, 1984). Tests with anionic paper, filter paper lined with iron oxide, have been brought to the attention of researchers (Gjorup et al., 1993). According to Silva & Raij (1996), this method showed a significant correlation with phosphorus absorbed by the sugar cane plant when applied to still soil, or rather, with the paper placed in contact with the humid soil. Although not the most efficient, it presented a significant degree of improvement considering the clay factor in multiple regression analysis. No one expects that a certain method of

extracting phosphorus from soil represents identically the capacity of a plant has to absorb phosphorus. New methods with universal characteristics are being tested so that losses in an increase of production through lack of fertilization or decrease of profits through excess of production may be avoided when more reliable methods are applied.

In their search for a method that better defines soil capacity to provide plants with phosphorus absorbed through diffusion, many authors tried to find a method that would define the latter factor (Silva & Raij, 1996; Gjorup et al., 1993; Rein, 1991). Consequently, the possibility of its usage in phosphate fertilization would be evaluated. Taking into consideration the fact that iron oxide irreversibly fixes the phosphorus through rapid kinetic reaction the above authors impregnated filter paper with iron oxide. Since iron oxide remained humid in contact with certain soils

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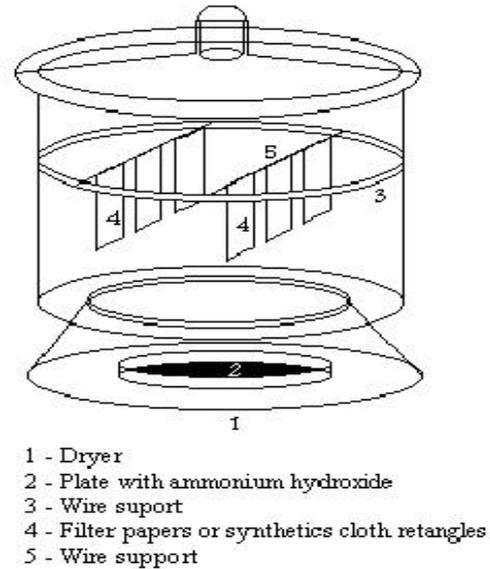
during certain periods of time, they fixed a certain amount of phosphorus. In principle this would represent the capacity of each soil to diffuse the phosphorus from a more concentrated region into a less concentrated one. Results obtained encouraged the authors to continue their analyses. The work developed by Rein (1991) was thus began, followed by research work in filter paper coated with iron oxide.

Based on these results and other works, Volkweiss and Corey (1988) in an unpublished report at the Federal University of Rio Grande do Sul, Brazil, discussed the possibility of using paper filter with iron oxide to define the necessity of phosphate fertilization.

## MATERIALS AND METHODS

### Preparation of phosphorus collectors:

Phosphorus collectors made from synthetic cloth received iron or aluminium oxide. The following sequence has been used for the preparation of collectors: a) cutting of cloth in 7.0 cm by 4.0 cm rectangles; b) decontamination of 4 or 5 rectangular pieces of cloth by washing with 0.2 mol.L<sup>-1</sup> sulphuric acid and rinsed with distilled and de-ionized water in a 100 mL beaker; c) distribution of decontaminated cloth on polyethylene film and drying at 45°C; d) treatment with 1.0 mL of a 0.4 M solution of FeCl<sub>3</sub>.6H<sub>2</sub>O and / or AlCl<sub>3</sub>, according to the type of collector desired; e) placing of polyethylene film and rectangular cloths for drying at 45°C; f) placing of cloth rectangles in a desiccator saturated with NH<sub>3(g)</sub> vapours (Fig. 1); the cloth rectangles are washed after a 12-hour period in the desiccator, with distilled and de-ionized water, in a polyethylene film and again dried at 45°C; h) cutting of dried rectangles by a punch into circles with 3.00 cm diameter. The same procedure was used for the preparation of collectors from filter paper. Decontamination was not needed. Collectors also received 0.5 mL of a 0.8 mol.L<sup>-1</sup> solution of FeCl<sub>3</sub> or AlCl<sub>3</sub>.



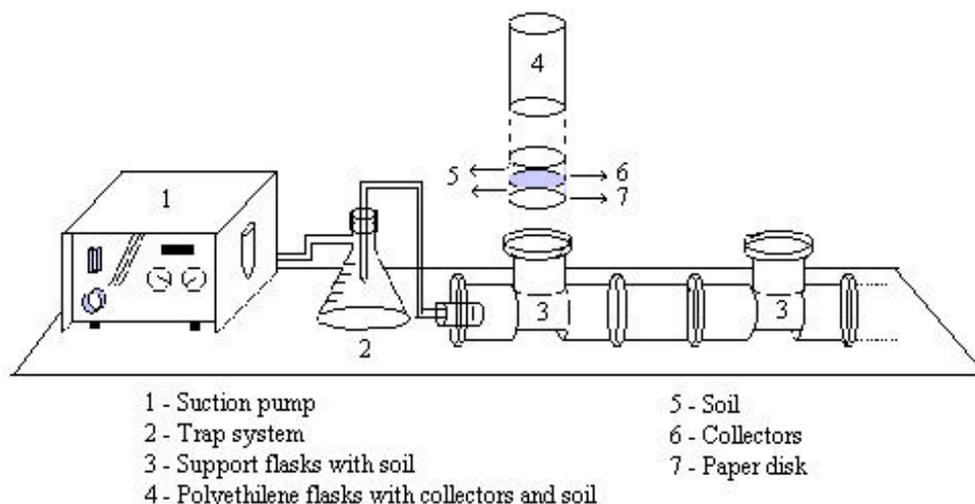
**Figure 1.** NH<sub>3(g)</sub> bath system used in the manufacture of collectors.

### Maximum fixation of phosphorus per collector:

Collectors were placed in 50 mL disposable cups and received a 2.0 mL solution of 0.0, 1.0, 3.0, 5.0, 7.0, 9.0 and 11.0 µg.mL<sup>-1</sup> of phosphorus. Five repetitions were performed during 12 h. Collectors were then washed with 40 mL of distilled and de-ionized water.

**Soils:** Four types of soils, found in the state of Paraná, Brazil, were used: LRd (Dystrophic “roxo” Latosol), LEd (Dystrophic Dark-Red Latosol), LBa (“Bruno álico” Latosol) and Ca (Cambisol). Soils were dried, ground, sifted with a 2 mm-aperture sieve and homogenized.

**Procedures:** Flasks of rigid plastic with 5.0 cm in height and 3.0 cm in diameter, were perforated by heated wire at the bottom with 12 small perforations. A filter paper was placed at the bottom of each flask together with a collector in a horizontal position and intercalated by two 3.5 mL portions of soil. Same procedure was carried for each of the type of soils, with three repetitions. Systems were placed in a Petry dish with 0.6 mm of distilled and de-ionized water. A certain amount of water was absorbed by the capillarity characteristic of each type of soil. Flasks were then taken to a vacuum system composed of a container for three samples (Figure 2) and linked to a 150 mmHg suction system.



**Figure 2** - Suction system with collectors in contact with soil

Suction was maintained for five minutes. Plastic flasks with collector and soil were kept still for 0, 12 and 24 h, respectively. Collectors were recuperated when plastic flasks were turned upside down on a clean surface. Collectors were taken out by tweezers and washed with distilled and de-ionized water from a pipette.

**Analysis of phosphorus in collectors:** The analytic determination of phosphorus followed the methodology of Murphy and Riley (1962) as developed by Rein (1991) and modified by the authors of this paper. 15.35 g of ammonium molybdate, 0.351 g of antimonitartarate of potassium and 43 mL of  $\text{H}_2\text{SO}_4$   $0.75 \text{ mol.L}^{-1}$  were dissolved in water up to 1 L. At the day of the use 1.352 g of ascorbic acid was dissolved for each 100 mL of the 1 L solution formerly prepared.

Digestion of iron oxide of collectors impregnated with phosphorus occurred by their immersion in 2 mL of  $\text{H}_2\text{SO}_4$   $0.75 \text{ mol.L}^{-1}$  for a period of 30 minutes in a 50-mL capacity cup. Distilled and de-ionized water (8 mL) was then added to the recipient completing the volume up to 10.00 mL. 1.00 mL of the complex was added to 10.00 mL of this extract. The sample was ready for phosphorus determination in spectrophotometer UV-VIS adjusted to wavelength 721 nm.

**Statistical analysis:** Variance analysis and Tukey's test were used for comparison of averages with SANEST software.

## RESULTS AND DISCUSSION

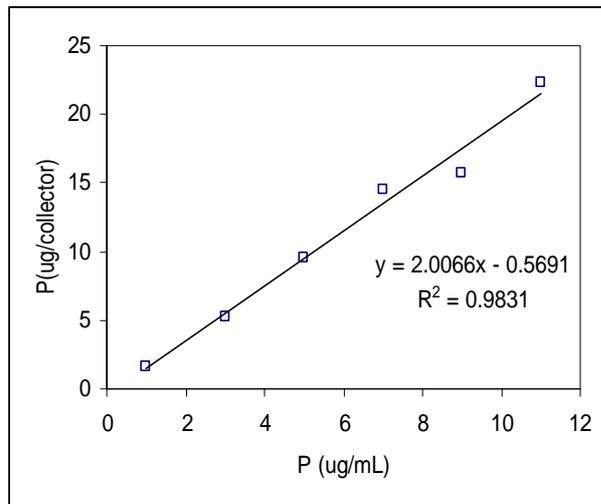
### Maximum fixation of phosphorus per collector:

Table 1 presents the concentrations of extracted phosphorus from 2 mL standard solutions tested and the result of the Tuckey's test for all collectors tested. With concentration band ranging from 0.0 to  $11.0 \mu\text{g.mL}^{-1}$ , results showed that total amount of phosphorus absorbed in collectors and phosphorus concentration in the solution had a significant correlation with variation of R between 0.9915 and 0.9986 for tests carried out with filter papers and synthetic cloth coated with iron oxide and aluminium oxide (Figures 3,4,5 and 6).

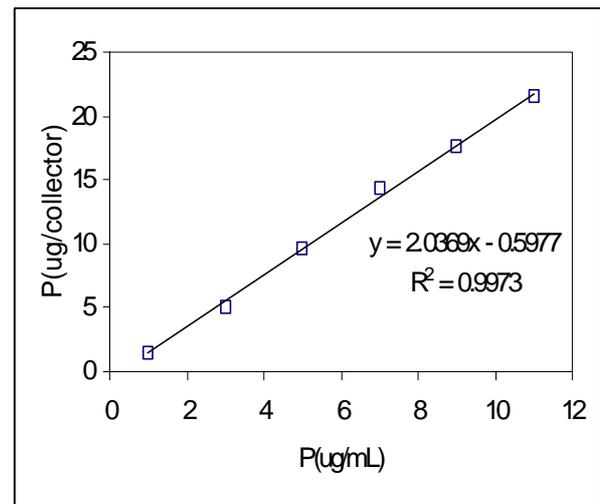
There was no significant difference between the percentage of phosphorus submitted to a 2 mL phosphorus solution with concentration changing from 0.0 to  $11.0 \mu\text{g.mL}^{-1}$  for all the collectors tested. At higher concentrations, this absorption was 103.3% and 101.6% in filter paper coated with iron oxide in 7.00 and  $11.0 \mu\text{g.mL}^{-1}$  concentrations, respectively and 102.3% in synthetic cloth coated with iron oxide. The explanation of this fact may have been the

contamination of collectors also observed through

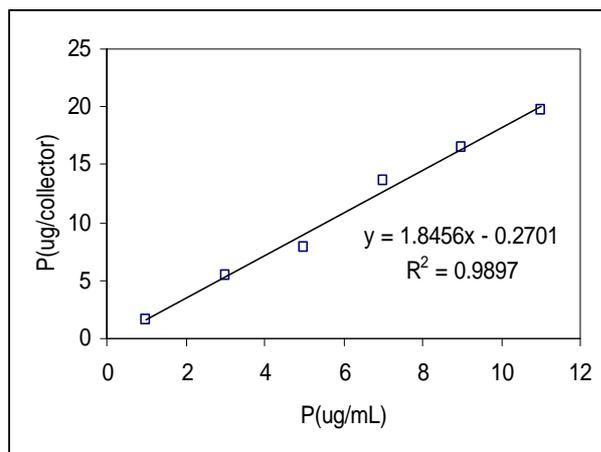
standard deviations.



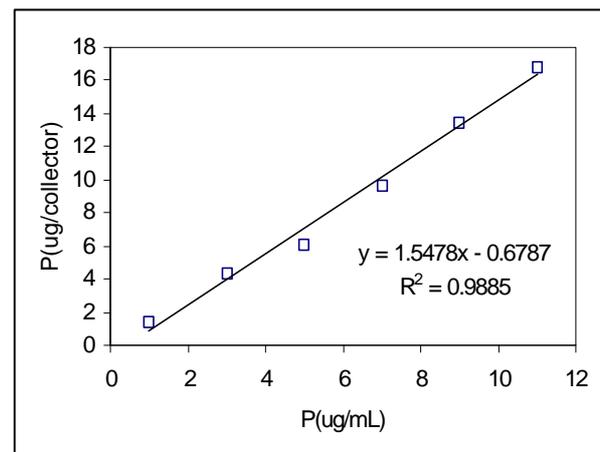
**Figure 3** - Amount of phosphorus extracted from filter paper collectors coated with iron oxide when in 2 mL solution of phosphorus with concentrations between 0.00 and 11.0  $\mu\text{g.mL}^{-1}$ .



**Figure 5** - Amount of phosphorus extracted by synthetic cloth collectors coated with iron oxide placed in 2 mL solution of phosphorus with concentrations varying between 0.00 and 11.0  $\mu\text{g.mL}^{-1}$ .



**Figure 4** - Amount of phosphorus extracted by filter paper collectors coated with oxide of aluminium in 2 mL solution of phosphorus with concentrations between 0.00 and 11.0  $\mu\text{g.mL}^{-1}$ .



**Figure 6** - Amount of phosphorus extracted by synthetic cloth collectors coated with aluminium oxide in 2 mL solution of phosphorus with concentrations between 0.00 and 11.0  $\mu\text{g.mL}^{-1}$ .

When solutions presented 0.0  $\mu\text{g.mL}^{-1}$  of phosphorus, variations of standard deviations occurred at intervals between 30.9 and 49.4%. Variations in samples with low quantities of P may be significant. Variations decrease when phosphorus concentrations are between 1.00 and 11.0  $\mu\text{g.mL}^{-1}$ .

Another factor that may be responsible for variations is the loss of small quantities of iron oxide from the external layer of the collectors during withdrawal from solution and washing of collectors. This would mostly interfere in the collectors with the more diluted solutions (Table 1).

**Table 1** - Concentration of phosphorus extracted, in  $\mu\text{g}/\text{collector}$ , from 2 mL standard solutions of 0.00 to 11.00  $\mu\text{g}\cdot\text{mL}^{-1}$  by filter paper and synthetic cloth collectors coated with iron oxide or aluminium oxide and result of Tukey's test for all the collectors tested.

Type of collector	Concentration of phosphorus in the 2 mL standard solution						
	0.00	1.00	3.00	5.00	7.00	9.00	11.00
pf Fe* (m)	0.1020	1.590	5.189	9.493	14.45	15.74	22.36
( $\sigma$ )	0.03240	0.140	0.1520	0.4780	1.003	0.5970	1.873
(%)	-	79.48 a	86.64 a	94.93 a	103.3 a	87.43 a	101.6 a
pf Al* (m)	0.08960	1.597	5.518	7.857	13.69	16.45	19.71
( $\sigma$ )	0.02810	0.1640	0.690	0.4060	0.9170	1.116	0.7010
(%)	-	79.87 a	91.96 a	78.57 a	97.79 a	91.40 a	89.57 a
px Fe**(m)	0.1160	1.529	5.021	9.691	14.32	17.62	21.56
( $\sigma$ )	0.03590	0.08600	0.2930	0.7040	0.3080	1.223	1.873
(%)	-	76.45 a	83.68 a	96.91 a	102.3 a	97.92 a	98.01 a
px Al**(m)	0.08850	1.357	4.330	6.061	9.620	13.42	16.86
( $\sigma$ )	0.04370	0.01100	0.6040	0.8380	1.252	0.3750	0.9840
(%)	-	67.86 a	72.17 a	60.62 a	68.71 a	74.51 a	76.65 a

L.D (Limit of Detection) of the used method was 0.025  $\mu\text{g}$  of phosphorus/collector (Welz, 1985); \* - filter paper collectors with iron oxide (Fe) or aluminium oxide (Al); \*\* - synthetic cloth collectors with iron oxide (Fe) or aluminium oxide (Al); m - average values;  $\sigma$  - standard deviations; % - percentages followed by same letter in the line do not differ among themselves at 5% by Tukey's test.

**Table 2** - Tukey's test for percentages of phosphorus fixed by collectors.

Variation source	Repetitions	material	% of P extracted	5%
Matrix (collector Support)	12	filter paper	90.21	a
		synthetic cloth	81.318	a
Substrate (type of oxide)	12	iron oxide	92.38	a
		aluminium oxide	79.14	b

L.D (Limit of Detection) of the used method was 0.025  $\mu\text{g}$  of phosphorus/collector (Welz, 1985); Averages followed by different letters in the row differ among themselves at 5% level of significance.

**Table 3** - Variance analysis for variation causes: soil (LBa, LEd, Ca, LRd)\*; collectors (synthetic cloth, filter paper); coating (iron oxide, aluminium oxide) and time of incubation (0.00 - 12.0 - 24.0 hours)

Source of variation	degree of freedom	sum of square	mean square
Soil	3	25.485	8.4950**
Collector	1	15.892	15.892**
Type of coating	1	1.9288	1.9288*
Time	2	37.028	18.514**
Soil vs. collector	3	3.3584	1.2195**
Soil vs. coating.	3	11.176	3.7254**
Soil vs. time	6	9.9442	1.6574**
Collector vs. coating	1	0.24305	0.24305
Collector vs. time	2	4.2299	2.1149**
Coating vs. time	2	0.86883	0.43441
Residue	119	25.964	0.21818
Total	143	136.42	

C.V. = 43.462%; \* = LBa (Latosol "Bruno álico"); LEd (Dystrophic Dark-Red Latosol); Ca (Cambisol); LRd (Dystrophic "Roxo" Latosol); \* = F, significative at 5% level of probability; \*\* = F, significative at 1% level of probability.

Phosphorus extraction from filter paper and from synthetic cloth, in phosphorus solutions between 0.0 and 11.0  $\mu\text{g}\cdot\text{mL}^{-1}$  did not have any significant difference. Both materials may be used for the manufacture of the collectors. However, the iron oxide was more efficient than aluminium oxide

since the former fixed a higher phosphorus average in the solution (Table 2). Although results showed the high capacity of phosphorus fixation by collectors, these were efficacious for diluted solutions up to 1  $\mu\text{g}\cdot\text{mL}^{-1}$ . It should be emphasized that the collectors manufactured with iron oxide

presented a characteristic colour which made possible the verification of the product's quality. This did not occur with collectors with aluminium oxide and the utilization of iron oxide in the manufacture of collectors might be considered at present more adequate.

**The performance of collectors in contact with the soils:** When collectors were in contact with the four types of soil, to evaluate their performance, variance analysis showed significant differences with regard to soils, to collectors made from synthetic cloth or filter paper, to iron oxide or aluminium oxide coatings and to interactions: soil vs. collector; soil vs. coating; soil vs. incubation time; collector vs. incubation time (Table 3).

**Table 4** - Phosphorus extracted by collectors with regard to soils (LBa, LEd, Ca, LRd).

Soil	N (repetitions)	Average	5%	1%
Led	36	1.6609	A	A
LRd	36	1.2840	b	B
LBa	36	0.72233	c	C
Ca	36	0.63169	c	C

L.D (Limit of Detection) of the used method was 0.025 µg of phosphorus/collector (Welz, 1985); Averages followed by different letters differ among themselves at 5% by Tukey's test.

**Table 5** - Phosphorus extracted from soil in µg/collector by collectors made of synthetic cloth and filter paper.

Substratum	N (repetitions)	average	5%	1%
synthetic cloth	72	1.4069	a	A
filter paper	72	0.74254	b	B

L.D (Limit of Detection) of the used method was 0.025 µg of phosphorus/collector (Welz, 1985); Averages followed by different letters differ among themselves at 5% by Tukey's test.

**Table 6** - Phosphorus extracted from soil in µg/collector by collectors with iron oxide and aluminium oxide coatings

Type of coating	N (repetitions)	Average	5%	1%
Fe oxide	72	1.1905	a	A
Al oxide	72	0.95901	b	B

L.D (Limit of Detection) of the used method was 0.025 µg of phosphorus/collector (Welz, 1985); Averages followed by different letters are different among themselves at 5% by Tukey's test.

Dystrophic Dark-Red Latosol had a greater capacity in liberating phosphorus. "Bruno álico" Latosol and Cambisol were similar and both liberated the least phosphorus (Table 4).

**Table 7** - Incubation time of collectors at 0.0, 12.0 and 24.0 hours

Incubation	N (Repetitions)	Averages	5%	1%
24.0 hours	48	1.6457	a	A
12.0 hours	48	1.6457	b	B
0.00 hours	48	1.6457	c	C

L.D (Limit of Detection) of the used method was 0.025 µg of phosphorus/collector (Welz, 1985); Averages followed by different letters differ among themselves at 5% by Tukey's test.

With regard to collectors made from filter paper or synthetic cloth, the latter was more efficient for extracting of phosphorus from soils (Table 5). The type of coating shows that iron oxide was more efficient in extracting phosphorus from soils (Table 6). Phosphorus collection increased with increased time of incubation (Table 7). Data indicated that the variation coefficient detected when collectors were placed in soils, 43.462% (Table 3), and showed high dispersion. Consequently, more tests are necessary to define new forms of placing collectors in contact with soils.

## CONCLUSIONS

1. Tests with collectors in phosphorus solutions were efficient for intervals between 1.00 to 11.00 µg.mL<sup>-1</sup>.
2. In contact with soils collectors made of synthetic cloth and coated with iron oxide were more efficient since they extract more phosphorus from the soil.
3. Collectors showed that their capacity in phosphorus collection was directly proportional to incubation time.

## RESUMO

Coletores de fósforo feitos de papel filtro e pano sintético (perfex) foram usados no estudo da determinação da necessidade de adubação fosfatada. Foram preparados coletores

impregnados com óxido de ferro e outros com óxido de alumínio. A capacidade foi testada colocando-os em 2 mL de uma solução padrão de fósforo (na forma de fosfato) com 0,0; 1,00; 3,00; 5,00; 7,00; 9,00 e 11,00  $\mu\text{g}\cdot\text{mL}^{-1}$ , depois foram colocados em contato com 4 tipos de solos (Lba, LRd, Led e Ca) e incubados por 0,0 e 24 horas. No teste, os solos foram mantidos com uma umidade equivalente a 150 mmHg de sucção. Os resultados mostraram que os coletores foram mais eficientes, na extração de fósforo, no solo LED e menos eficiente no LBa e Ca (Cambissolo). O pano sintético foi a matriz (material suporte) que proporcionou melhores resultados. O óxido de ferro foi o substrato foi o mais adequado. O teor de fósforo extraído é função direta do tempo de incubação.

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