MASKING EFFECT AND PRECIPITATION
OF DIFFERENT VEGETABLE TANNING AGENTS WITH METALIC SALTS

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Abstract: There are two main aims in this work, firstly the replacement of the non-ecological chemical chelates, used in plants nutrition as oligoelements, by biodegradable tannin chelates. And secondly, precipitation and removal of Quebracho, Chestnut and Mimosa with metallic hydroxide.

Key words: Vegetable Tanning agents, metallic salt, masking effect

1. INTRODUCTION

Tannin extracts are complexes mixtures of polyphenolic substances. The tannin extract solutions contain the **non-tannin** and the **tannin,** the latter are able to combine and stabilize hide collagen fibers. Tannins in solution have different molecular weight and they could be found in form of colloidal micelles, aggregates or forming bigger particles that precipitate.

The vegetable extracts are classified in two principal groups:

1.- Condensed or catechinic tannins, based in the catechin

2.- Hydrolysable or pyrogallics tannins

In Figure 1, the chemical composition of the two types of vegetable tannins is enclosed.

When the extract concentration, temperature, or pH solutions are modified or when neutral salts are added, the balance is modified and consequently precipitation of vegetable extract occurs, specially the tannin part. Trivalent metal salts form basic salts; at the same pH medium, chromium sulfate solutions are more soluble than aluminium and these more than iron, taking into account Figure 2.

In order to simplify the present study, it has been divided in two different works; the first one consists on chelate formation between the metallic ion and the vegetal tannin extracts in order to prepare biodegradable metallic chelates by mixing metallic ions with tannin extracts and secondly the elimination of the tannin from vegetable extract effluent by absorbing it in an insoluble metallic hydroxide.

Figure 1. Chemical composition of the two types of vegetable tannins

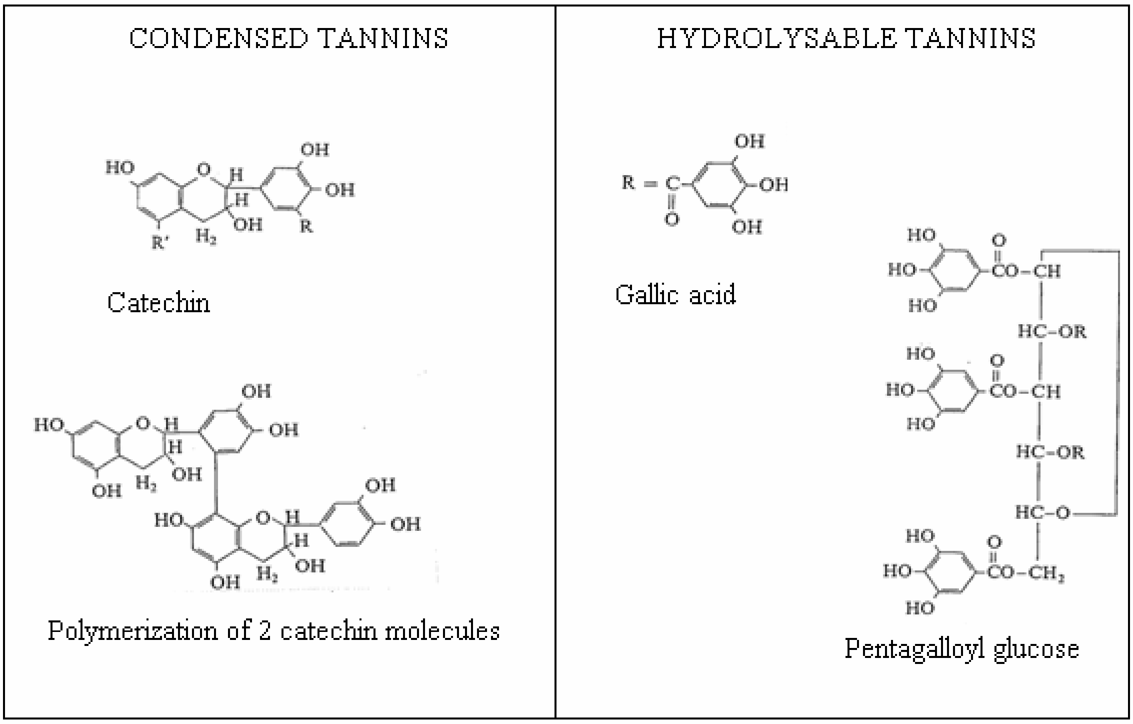
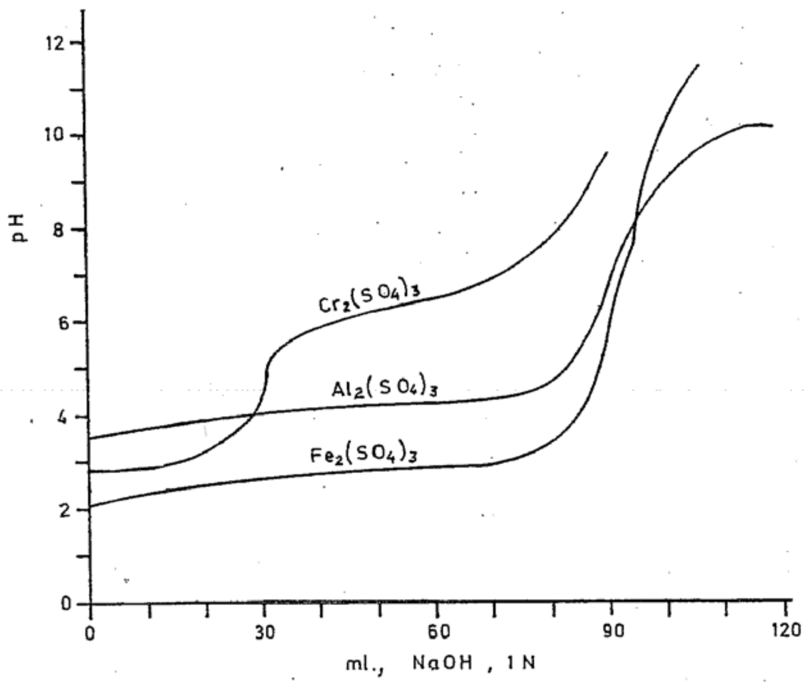


Figure 2. Titration of metallic salts with sodium hydroxide vs pH.



2. EXPERIMENTAL SECTION

Along the present study, the commercial extracts used were:

- Quebracho from Indunor ATO; with a tannin content of 77,9%
- Chestnut from Dulcotan-Silva, with a tannin content of 71,8%
- Mimosa Me, with a tannin content of 79,5%

The tannin extract contents were determined according to the filter method using slightly chromated powder hide.

The metallic salts tested were the following:

- A 40% ferric chloride solution (commercial product)
- Aluminum sulphate, crystallized with 18 water molecules (reactive product)
- Basic chrome sulphate, 33.3 basicity 23 % Cr_2O3 (commercial product)

2.1. *CHELATE FORMATION BETWEEN METALLIC IONS AND VEGETABLE TANNINS*

To evaluate the chelating capacities of the metallic salts with vegetable extracts, different solutions were prepared maintaining constant the amount of vegetable extract and changing the amount of metallic salts. In all cases, two control solutions were prepared, one corresponding to the vegetal extract alone (C1) and the other containing the metallic ion alone (C2). They were taken as reference for the COD and the metal ion maximum concentrations, respectively.

In the following tables the solution compositions, expressed in grams, are detailed.

			Iron				**Aluminium**				**Chromium**			
	C-1	**C-2**	**I**	**II**	**III**	**IV**	**I**	**II**	**III**	**IV**	**I**	**II**	**III**	**IV**
Me Sol[1]	---	6	8	6	4	2	16	12	8	4	20	16	12	8
Extract	12	--	12	12	12	12	12	12	12	12	12	12	12	12
Water	88	94	80	82	84	86	72	76	80	84	68	72	76	80

[1] Me sol corresponds to the 40% metallic solution amount

The chelate stability was studied by diluting one volume of each solution with 200 tap water volumes and by observing the solubility, the stability of the new formed chelate as well as the UV spectra.

2.2. ELIMINATION OF THE TANNIN EXTRACT IN SOLUTION FROM A WASTE BATH

Different metal solutions (iron, aluminum and chromium) with three different vegetal extracts were prepared in order to evaluate the extract absorption capacity of the metallic hydroxides. The amount of vegetable extract was kept constant while the amount of metallic salt solution was changed as well as the amount of potassium hydroxide. In the following table the prepared mixtures are shown, with the amounts expressed in grams.

		Ferric hydroxide			Aluminium hydroxide			Chromium hydroxide		
	Control	**I**	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**
KOH 85%	---	4	3	1,5	2	1,5	0,75	2,6	1,7	0,86
40% metal sol	---	8	6	3	8	6	3	15	10	5
Veg. extract	1	1	1	1	1	1	1	1	1	1
Water	99	87	90	94,5	89	91,5	95,25	81,4	87,3	93,14

In order to observe if the formed chelates were stable under dilution, the solutions were diluted 1/200 with tap water, and then the UV spectra recorded.

3. RESULTS

3.1 *CHELATE FORMATION BETWEEN METALLIC IONS AND VEGETABLE TANNINS*

In these trials the most important values are the pH and Chemical Organic Demand (COD) as well as the metal concentration in solution. In the next tables, the results are reported, where COD is expressed in g O_2/L and the metal concentration in g /Kg.

Ferric Chloride

		Quebracho					Chestnut					Mimosa				
	C2	**C-1**	**I**	**II**	**III**	**IV**	**C-1**	**I**	**II**	**III**	**IV**	**C-1**	**I**	**II**	**III**	**IV**
pH	1,6	4,7	0,8	1	1,2	1,8	3,4	0,7	0,9	1	1,5	4,8	0,9	1,0	1,2	1,9
COD	---	173	129	154	127	176	140	132	133	155	129	183	56,2	101	135	163
Fe	8,2	---	11,4	8,7	4,3	3,0	---	9,8	8,0	7,0	2,8	---	11,6	8,6	4,7	2,4

Aluminum Sulphate

		Quebracho					Chestnut					Mimosa				
	C2	**C-1**	**I**	**II**	**III**	**IV**	**C-1**	**I**	**II**	**III**	**IV**	**C-1**	**I**	**II**	**III**	**IV**
pH	3,3	4,7	3,0	3,1	3,1	3,2	3,4	2,2	2,2	2,3	2,3	4,8	2,8	2,8	2,9	2,9
COD	---	173	195	175	169	175	141	128	143	131	135	183	181	177	173	185
Al	4,0	---	5,0	3,9	2,5	1,3	---	5,4	3,7	2,6	1,2	---	5,6	3,9	2,8	1,4

Basic Chromium salt

		Quebracho					Chestnut					Mimosa				
	C2	**C-1**	**I**	**II**	**III**	**IV**	**C-1**	**I**	**II**	**III**	**IV**	**C-1**	**I**	**II**	**III**	**IV**
pH	2,9	4,7	2,6	2,6	2,7	2,7	3,4	1,9	2,0	2,0	2,1	4,8	2,3	2,3	2,4	2,4
COD	---	173	190	191	187	183	140	159	148	145	150	183	192	187	190	184
Cr	9,2	---	15,0	11,9	9,3	6,1	---	17,1	11,6	9,2	6,2	---	14,9	12,2	9,3	6,0

According to the above results:

With ferric chloride:

As the pH of $FeCl_3$ solution is very acid, resulting solution pHs are also very acid.

- With Quebracho extract, the organic matter that remains in solution increased as the ferric chloride amount decreases. Consequently, the COD amount increases as the pH of the solution also increases and the precipitate observed decreases. The COD value in solution IV is closed to the Control value.

  With Chestnut extract, the COD remains practically constant in the different solution; which indicates that the $FeCl_3$ does not precipitate with Chestnut.

  The Mimosa extract precipitates much more than the other studied extracts. This precipitation decreases as the $FeCl_3$ amount decreases; which corresponds to a pH increase. Consequently, it is observed a COD increase from solution I to IV. The Mimosa extract solution behavior is closed to the Quebracho extract one.
- In all these assays, the iron amount in solution decreases as the quantity of $FeCl_3$ added is also reduced.
- According to stability dilution trials and UV-spectra it can be stated that:
  - The solution pHs are in the range 5,9-7,3;.no significant differences in pH are observed.
  - No precipitation are observed in Quebracho solutions when diluted with tap water
  - Total precipitation is observed with Chestnut (solution I, II and III) and with Mimosa (solution I and II). In the rest of solutions, no precipitation is observed.
  - In Chestnut and in Mimosa solutions, as the amount of precipitate increase, lighter are the resulting solutions

  It can be confirmed that iron forms chelates with all these extracts, being the strongest those with Quebracho, as no precipitation is observed when changing the pH of the solution.

With Aluminum Sulphate:

The solutions are less acidic than those with $FeCl_3$.

The observed precipitation when mixing the Chestnut extract with aluminium ion is insignificant. Consequently, not only the extract but also the aluminium remains in solution.

According to stability dilution trials and UV-spectra it can be stated that

No one of the tested extracts form chelates with aluminium. Moreover, the mixture of vegetable extract and aluminum salt remain in solution.

- It is observed high turbidity in Chestnut (solutions I and II) and Mimosa (solutions I, II and III). With Quebracho (I, II), Chestnut (III, IV) appears light turbidity and no precipitation at all is observed in the rest of solutions. The solutions become lighter as the amount of turbidity increase.

With Basic Chromium salt

No significant precipitation is observed when mixing the extracts with chromium ion. Consequently, not only the extract but also the chromium remains in solution.

According to stability dilution trials and UV-spectra it can be stated that:

No one of the tested extracts form chelates with chromium. Moreover, the mixture of vegetable extract and aluminum salt remain in solution.

Total precipitation is observed with Chestnut and with Mimosa (solutions I and II), and abundant precipitation in Chestnut ad Mimosa.(solutions III and IV). No precipitation is observed, nor in Quebracho, neither in Chestnut and Mimosa (solution IV and Control).

3.2. ELIMINATION OF THE TANNIN EXTRACT IN SOLUTION FROM A WASTE BATH

After their preparation, the solutions were filtered to eliminate the precipitate. Precipitate amount, pH, conductivity, COD value as well as metal concentration in final solution were determined.

From all of these values the principal value is the COD, as it gives information about the remaining extract in solution. Consequently in next table, and in order to simplify the results, only the COD in the filtered solutions are enclosed.

COD (g O_2/L)		**Ferric Hydroxide**			**Aluminum Hydroxide**			**Chromium Hydroxide**		
	Control	**I**	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**
Quebracho extract	14,0	0,7	2,4	5,7	1,8	4,7	6,8	6,0	11,5	13,4
Chestnut extract	10,7	0,7	1,6	2,5	2,2	2,4	4,4	5,1	6,2	8,7
Mimosa extract	13,6	2,1	1,7	4,9	2,5	2,3	7,2	5,5	8,7	13,2

According to these trials, the ferric hydroxide eliminates better the vegetable extracts than the aluminum hydroxide and these more than the chromium hydroxide. There are not significant differences among the three extracts used in front of the same metal hydroxides.

4. CONCLUSIONS

To form metallic chelates is necessary acid pH and high amounts of vegetable tannin.

With aluminium and chromium salts, no detected metallic chelates are formed with the vegetal extracts in the assayed conditions. Moreover, the metals remain in solution.

If the proportion between the weight of Quebracho extract and the ferric chloride 40 % solution is higher than one and the pH is not changed, a complex Fe-tannin is obtained. That complex is stable when diluted 1:200 with tap water.

When metallic salts are mixed with extract solutions, even in the most favorable conditions, it is form a precipitate. This could be due to salinity increase or that some extract compound precipitate with the metallic ion.