STUDY CONCERNING OF MODIFICATION OF SPRUCE WOOD BARK BY HYDROXYMETHYLATION REACTION

CERCETĂRI CU PRIVIRE LA MODIFICAREA COJII DE MOLID PRIN REACŢIA DE HIDROXIMETILARE

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Abstract. *This work presents a study about reactive extraction of spruce bark by successive treatment of these with an ammonia solution, followed by the hydroxymethylation reaction with formaldehyde and condensation with urea. Products resulting from changes made have been tested for toxicity. For modified and unmodified spruce bark as well as for the products resulting from the extraction were conducted in laboratory tomato plants growing experiments on hard sand. Experimental data showed statistically significant differences according to the sequence of reactions applied to the results of germination experiments. For the sequence of reactions involving the extraction of the shell under the action of ammonia and urea formaldehyde, the results support the recommendation for use as a plant growth stimulator or to obtain slow-release fertilizer*.

Key words: spruce bark, hydroxymethylation, extraction, toxicity, tomato plants.

Rezumat. *Lucrarea prezintă un studiu privind extracţia reactivă a cojii de molid prin tratarea succesivă a acesteia cu soluţie de amoniac, urmată de reacţia de hidroximetilare cu aldehidă formică şi condensare cu ureea. Produsele obţinute în urma modificărilor efectuate au fost testate din punct de vedere al toxicităţii. Pentru coaja nemodificată, modificată precum şi produsele rezultate în urma extracţiei s-au realizat în laborator experimente de cultivare a plantelor de tomate pe suport de nisip. Datele experimentale au evidenţiat diferenţe semnificative statistic funcţie de secvenţa de reacţii aplicate pentru rezultatele experimentelor germinative. Pentru secvenţa de reacţii ce implică extracţia cojii sub acţiunea amoniacului, aldehidei formice şi ureei, rezultatele susţin recomandarea de utilizare ca stimulator al creşterii plantelor sau pentru obţinerea de îngrăşăminte cu eliberare lentă.*

Cuvinte cheie: coajă de molid, hidroximetilare, extracţie, toxicitate, tomate.

INTRODUCTION

Under conditions of intensive cultures in agriculture and forestry, chemical fertilizers have become a valuable means for achieving increased vegetal production. The necessity of organic amendments has increased along

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with mineral fertilizer consumption. In order to satisfy such increasingly bigger requirements, and ameliorate some physical and chemical soil properties, there are a few products used, from which we remind, aside from compost, coal of various origins and composts from vegetal remains. A vegetal waste source, insufficiently capitalized until this day and taken into consideration only at obtaining compost, is represented by the bark and sawdust originating in forestry exploitations and wood processing industry (Stoica L. et al., 1968).

These subproducts can be used in agriculture thanks to the increased content of nutritive elements useful to plants. On the other hand, the bark amounts that are capitalized in the tenant industry are small reported to those that are being produced on a daily basis. Trying to deposit in halls of big dimensions may often lead to spontaneous ignitions, but transporting bark from the inside of the factories is also inhibited by the profitableness barrier, so that this waste becomes a material regarded as disadvantageous in an enterprise administration (Petrovic S., 1979).

Appreciating the bark amounts that result in each year in our country accurately is a difficult task, since the bark amount in industrial wood, reported to the total of raw wooden mass, varies along with the species and the volume of wood taken into processing. One of the simplest ways of using bark waste is their conversion to soil fertilizing and conditioning agents. Analysis of specific data highlights the fact that wood bark presents chemical products with complex structures, from which polyphenolic types are of particular interest. Spruce fir bark is characterized by high polyphenolic compound content (approx. 4.5% compared to only 2.5% in deciduous tree bark) and it is accessible due to processes of mechanical and chemical capitalization of wood.

Treating bark by various means with the goal of enriching its nitrogen content and placing it in the soil presents more advantages from several viewpoints especially where intensive soil exploitation can lead to economically justified harvests (Simionescu C.I. et al., 1989). Considering the contribution of vegetal materials and implicitly of wood bark in the forming of humus, the modification of the latter becomes of interest for efficient usage and as a support for the transport of a nitrogen source. The problem becomes more important when the nitrogen source is represented by urea, which is characterized by increased solubility, hence the risk of it descending in the soil with phreatic water before manifesting its fertilizing agent properties (Dumitru M. et al., 2003, 2006). Previous experiments have shown that there are to be found in bark important amounts of polyphenols with biostimulating role within plant germination and growth and natural products with aromatic structure (polyphenols and lignin) can react with formaldehyde and urea (Căpraru A.M. et al., 2010, Măluţan Th. et al., 2007). For these reasons, in the present study we have analyzed the possibility of applying a reactive extraction that may allow capitalization of the whole content of bark and polyphenols, along with coupling these with urea through a condensation reaction.

MATERIAL AND METHOD

The following materials have been used:

- crumbled spruce fir bark (industrial provenience)
- ammonia solution of 3% concentration
- formaldehyde solution of 37% concentration
- urea.

Work procedure: Spruce fir bark was subjected to successive treatments with ammonia solution, formaldehyde and urea as found in the scheme presented in figure 1:

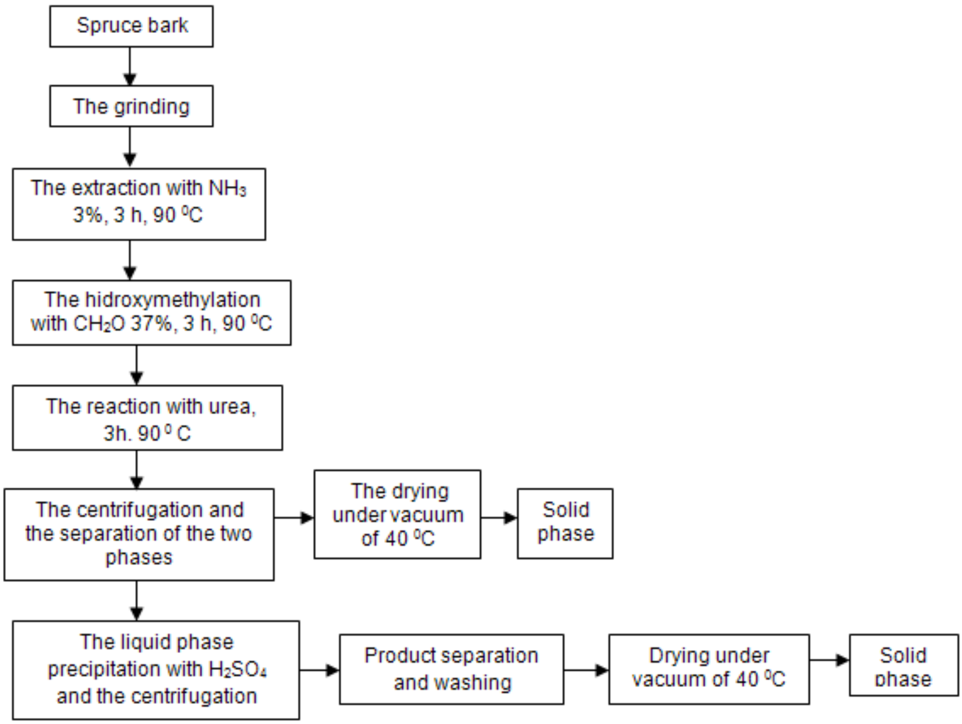

Fig. 1 - Scheme of the reactive extraction of spruce fir bark

Procedure: 5 g of completely dried (U=11.23%) spruce fir bark were introduced in a 250 ml glass reactor with three necks and treated with 3% concentrated ammonia solution on a three hour duration at 90° C under mechanical agitation. Then the reaction was continued with formaldehyde and urea for three hours, at the temperature of 90° C, under agitation.

The experiments have been performed in the following versions:

1. In the first experiment the spruce fir bark was treated with 3% concentrated ammonia solution, at the temperature of 90° C for a three hour time span, and the resulted product was centrifuged at 2500 rpm for 10 minutes, then the liquid phase was separated by the solid one and subjected to drying at 40° C. The resulted supernatant was precipitated with sulfuric acid solution of 1N up to 2 pH. After precipitation, the suspension was subjected to centrifugation for 10 minutes at 2500 rpm, and then the separated products were washed, centrifuged, and dried again.

2. In the second experiment the spruce fir bark was treated with ammonia solution (under the conditions of the first experiment), then formaldehyde solution of 37% concentration was added. After the reaction, the products were separated through centrifugation at 2500 rpm and precipitation.

3. In the third experiment spruce fir bark was treated with a solution of ammonia, formaldehyde and urea. Bark that had been modified under conditions of the second experiment was treated with urea. In this case, the reaction took place at the temperature of 90°C for three hours under agitation. Resulted products were centrifuged at 2500 rpm for ten minutes, then the liquid phase was separated and the solid phase was dried at 40° C. The resulted supernatant was precipitated with sulfuric acid solution of 1N up to 2 pH. After precipitation the suspension was subjected to centrifugation for 10 minutes at 2500 rpm, the resulted product was washed, centrifuged and dried. Products resulted from reactive extraction of spruce fir bark (extracted bark and fraction recovered through precipitation) were tested in order to determine their influence in tomato plant growth. Tests were performed in pots with sand in which 1 gram of treated/untreated bark (with 1 g of precipitate) was added, the witness sample consisting of sand. In each pot were seeded three tomato seeds, irrigated daily with 5 ml of water, while keeping track of the germination and development of plants in the presence of bark and products separated by reactive extraction. The germination of seeds and the evolution of tomato plants were analyzed at 7 days periods within a 3-week interval, by measuring the height. Experimental data were statistically processed with the aid of the *Unscrambler* application.

RESULTS AND DISCUSSIONS

Introducing urea in the reaction environment allows for its interaction with methylolic groups, blocking the possibility of their condensation at the same time. The extraction efficaciousness of the reaction in this case is smaller due to a possible condensation with the participation of hydroxymethylolic groups introduced both in solid phase and dissolved polyphenolic products. Under these conditions, urea can bind with the solid sublayer as well as the products from the liquid phase, with an increased value of the extraction efficaciousness. As for the usage of modified products, these were tested in order to highlight their influence over the growth and development of tomato plants

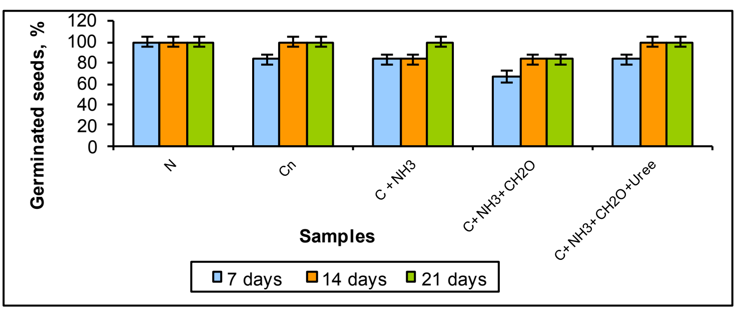

Fig. 2 – The variation of capacity of germination for seeds tomato

N- sand (witness sample); Cn – untreated bark; C+NH_3 – bark treated with ammonia solution; C+NH_3+CH_2O – bark treated with ammonia solution and formaldehyde; C+NH_3+CH_2O+Urea – bark treated with ammonia solution, formaldehyde and urea.

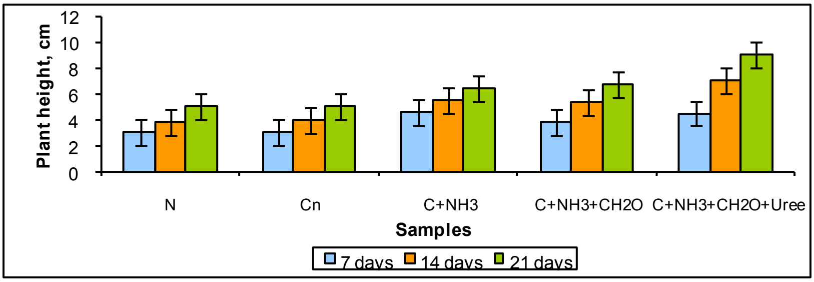

Fig. 3 - Variation the height of tomato plants

In figures 2 and 3 is presented the germination capacity and height variation of tomato plants on a three week time span, treated with bark resulted from centrifugation of the product obtained at extraction.

In figures 4 and 5 is presented the variation of germination capacity and height of tomato plants for a three week timespan, in pots in which precipitates resulted from reactive extraction of spruce fir bark were introduced.

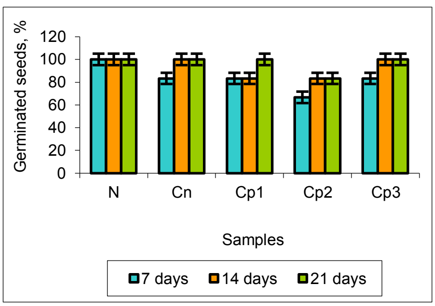

Fig. 4 - The variation of capacity of germination for seeds tomato

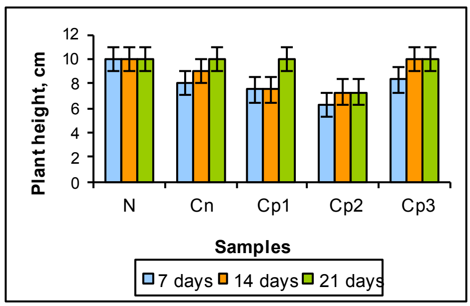

Fig. 5 - Variation the height of tomato plants

N – sand (witness sample); Cn – untreated bark; Cp1 – precipitate resulted from bark treated with ammonia; Cp2 – precipitate resulted from bark treated with ammonia and formaldehyde; Cp3 – precipitate resulted from bark treated with ammonia, formaldehyde and urea.

It was noticed that products resulted in the third version of bark treatment ensures a light stimulation of tomato plant growth determined by the presence of urea. In the case of bark treatment with ammonia and formaldehyde, tomato plant growth is slower and even drying is noticed in a relatively short time. After 21 days, the obtained results were evaluated and we reached the conclusion that favorable effects regarding the growth and development of tomato plants are present in the pot where spruce fir bark treated with ammonia, formaldehyde and urea was introduced.

CONCLUSIONS

1. The extraction of spruce fir bark in which the action of ammonia combines with that of formaldehyde and urea can be recommended in order to obtain components destined to composite structures used in stimulation of growth and development of plants.

2. Data obtained in germination experiments in pots on sand support – as well as those of plant cultivation in the presence of modified products, recommends capitalization of spruce fir bark with the purpose of acting successfully as fertilizer in agriculture.

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