

# Polymer Nanoparticles: Adsorption and Desorption of the Weedkiller Tebuthiuron Turned to Green Chemistry

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## Abstract:

The herbicide Tebuthiuron is one of the main responsible for controlling and combating weeds in sugarcane plantations. Its degree of toxicity and its half-life are the main factors for the degradation of the environment. In order to reduce the amount of product used, an anchoring study of the herbicide in polymeric nanospheres was carried out to study the degree of controlled release, observing factors such as conductivity and pH variation. The results of conductimetric titrations and UV analysis in the visible region showed the efficiency of the chitosan nanospheres in the controlled release process of the herbicide, demonstrating that the best pH range for release is from 6.3 to 7.2. This study is a precursor of new activities that will guide further research to work on reducing the half-life of Tebuthiuron, reducing production costs and preserving the environment.

**Keywords:** tebuthiuron; adsorption; chitosan; desorption; nanoparticles

## 1. Introduction

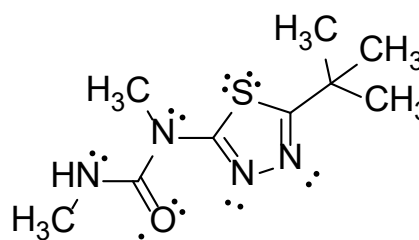
The use of agricultural pesticides and the increase in the production of innumerable varieties of vegetable crops triggers a scenario of environmental chaos. The uncontrolled use of herbicides and the lack of inspection are points that favor the advance of environmental degradation.

According to Pires et al. [1], herbicides are the most commonly used pesticides in agricultural activity, being used in large areas. To reduce labor costs and speed up production, farmers use an excessive amount of herbicides.

The availability of these molecules (herbicides) in the soil, promotes the adsorption and absorption processes, known as sorption, leads to reduced fertility and increased soil degradation, causing soil contamination of the leaves and seed germination [1].

Sugarcane crops, the main herbicide used is Tebuthiuron 1- (5-tert-butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea (Figure 1) of a systemic

herbicide, absorbed by the leaf of the weed, much used in pre-emergence and post-emergence treatments. The half-life of an herbicide depends on its composition, soil type, amount of organic matter present, among others, in the case of Tebuthiuron, its half-life is 360 days and can be found in the soil up to 2 years after its application. Tebuthiuron has a high solubility in water, about 2,500 mg.L<sup>-1</sup>, this solubility can be defined as the amount of herbicide that dissolves in pure water at a given temperature [2-4].



**Figure 1.** Chemical structure of Tebuthiuron [3, 4].

Chitin is one of the most abundant polysaccharides in nature, being behind only

cellulose, can be extracted from the exoskeleton of crustaceans, insects and the cellular be present of some fungi [5]. Chitin consists of 2-acetamido-2-deoxy-D-glucopyranose units linked by  $\beta$ - (1  $\rightarrow$  4) bonds.

Partial deacetylation of the chitin polymer chains occurs by alkaline treatment, thus giving rise to chitosan. Some properties of chitosan, such as viscosity, degree of deacetylation, molar mass depend on sources of raw material and manufacturing methods [6].

The polyacrylic nature of chitosan can be obtained by acid dissolution in various ways, so abrupt change of pH will promote the formation of spheres, microspheres, nanospheres or gel. In controlled release systems, there are great advantages in the use of nanoparticles, which are divided into nanocapsules and nanospheres that differ due to their structural composition. The

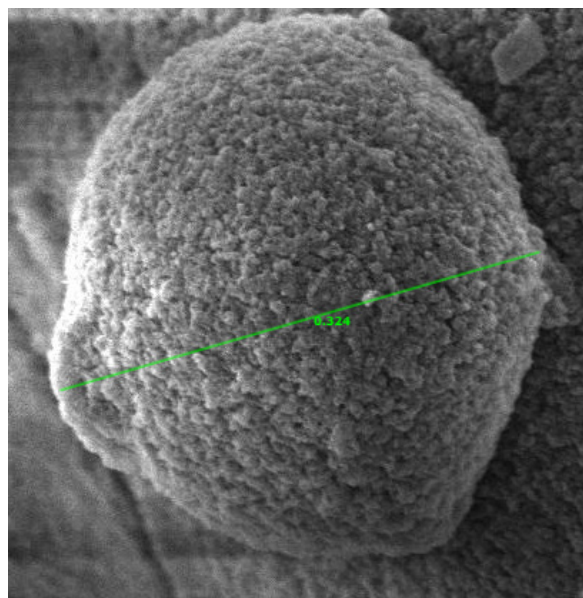
use of a controlled release system represents one of the frontiers of science, to the benefits offered as progressive and controlled release of the material, the longer exposure time promotes a controlled effect for different applications within materials science [7].

The objective of this work was to evaluate the behavior of the herbicide Tebuthiuron anchored in chitosan nanospheres, with the aim of finding higher pH ranges for more efficient applications in the agricultural environment.

## 2. Results and Discussion

### 2.1- MEV characterization

The nanoparticles presented varied size within the nanoscale, from 0.23 to 0.58 nm, according to Figure 2.



**Figure 2.** Morphology nanoparticle chitosan (0.23 – 0.58nm).

### 2.2 - Conductimetric Titration

The interactions that occur on the surface of the nanoparticle can be proven due to the change in conductivity with increasing pH.

The increased availability of ionizable cations and anions in solution promotes the release of the molecule of interest from the surface of the nanoparticles.

This phenomenon occurs due to the electronic exchange between the surface of the

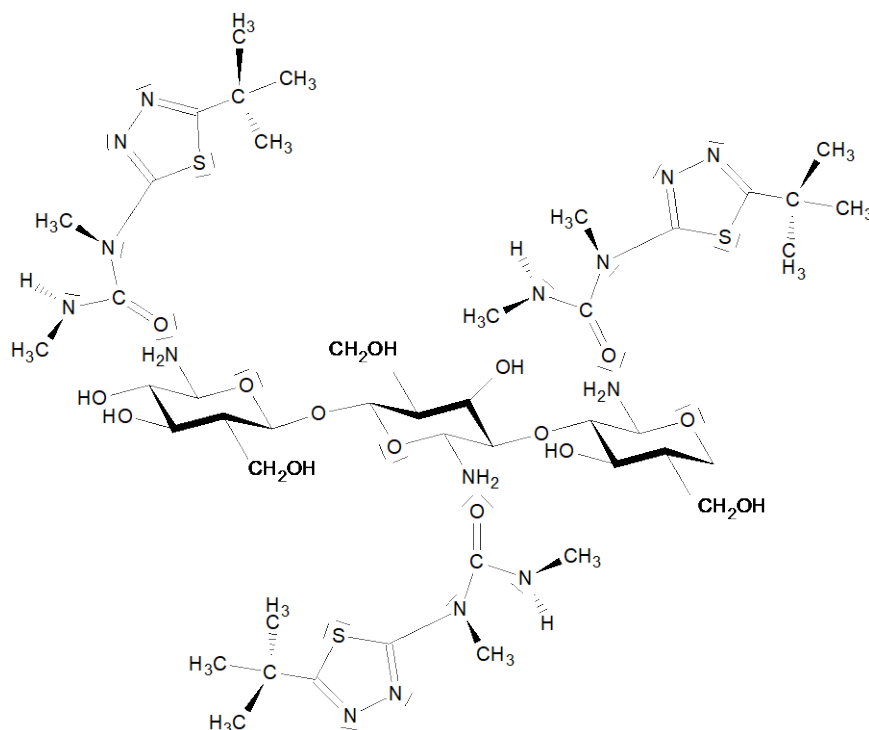
polymer (adsorbent) and the molecule of interest (adsorbent). Figure 1 represents the structure of the Tebuthiuron molecule, where amine and oxygen groups are strongly concentrated electrons. In these regions the interactions with the surface of the polymer occur that are later turned off with the increase of the pH.

During the additions of the NaOH solution, due to the protonation and deprotonation effect, the Tebuthiuron molecules desorb the surface of the nanoparticle, until there is a balance between

the protonated and deprotonated species.

With the pH adjustment of 6.3 to 12, it is observed that an increase in the availability of chitosan  $\text{NH}_2^-$  deprotonated groups, due to the detection of new conductivity peaks, which represent the availability of active ionic sites able to promote interactions.

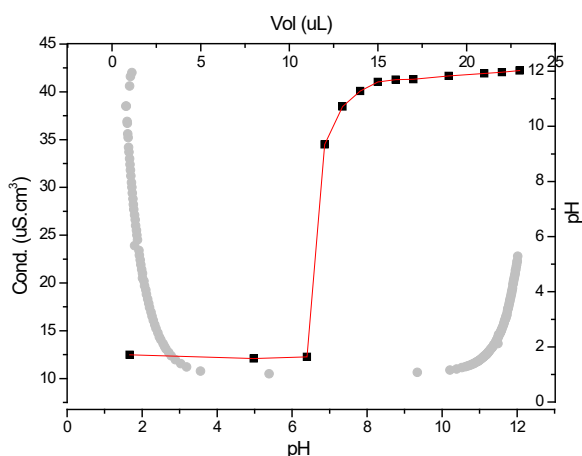
Thus, interaction with the herbicide binding groups is likely to be more difficult, allowing weak interactions of the Van der Waals type (Figure 3), with physical characteristics overlapping chemical bonds occurring in the acid medium forte.



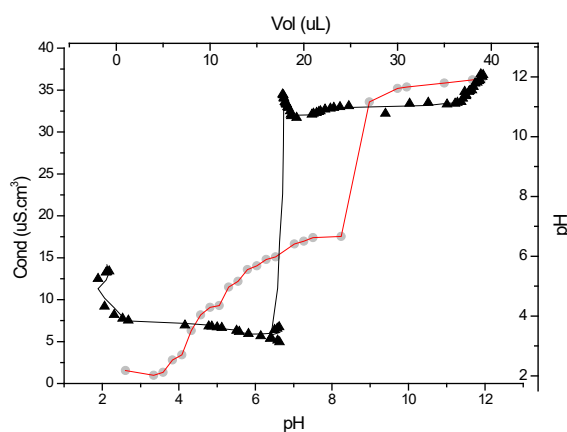
**Figure 3.** Probable adsorption mechanism of Tebuthiuron in chitosan nanoparticle.

This factor helps us to interpret the behavior of the Tebuthiuron molecule (in red in Figure 4) where it is perceived that the increase of pH directly influences the increase of available ions in solution.

When comparing with this interpretation titration with nanoparticles made of chitosan and Tebuthiuron molecule (Figure 5), there is the same behavior, where the pH vs. conductivity peaks are higher when they reach a basic pH.



**Figure 4.** Tebuthiuron conductivity titration.



**Figure 5.** Tebuthiuron and chitosan conductivity titrations.

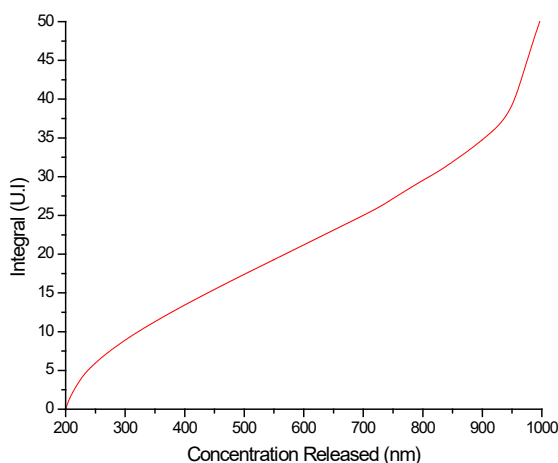
Another factor that we can mention is that there is a direct correlation between increased availability of  $\text{NH}_2^-$  groups and injections of hydroxyl groups in the middle. Changing the equilibrium of the solution promotes the release of ions bound to the Tebuthiuron molecule, increasing the availability due to the desorption process.

### 2.3 – UV-Vis characterization

The samples were collected to determine the adsorptive capacity of the herbicide and analyzed at the wavelength of 257 nm. According to Figure 4, the peaks with the highest ion exchange intensity remained in the pH range of 6.3 to 7.2.

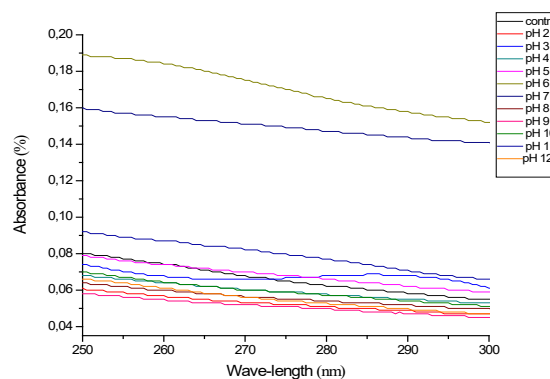
After the UV-Vis analyzes, it was observed that the release characteristic was maintained, elucidating the probable reaction mechanism proposed in Figure 3.

Figure 6 shows the integration conductance peaks controlled release of the Tebuthiuron molecule with increasing the pH range within the points of greatest release.



**Figure 6.** Integration of higher ionic conductivity peaks in UV-Vis analyzes.

The change in Tebuthiuron concentration in the titrated solution in the best controlled release range is directly correlated with the peaks identified in Figure 7 where they are highlighted with higher peak absorbance in the pH range of 6.3 to 7.2, evidenced in Figure 6, highlighted in the pH points 6 and 7.



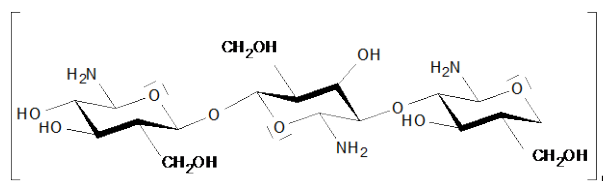
**Figure 7.** UV-Vis analysis Tebuthiuron, highlighting the point of analysis pH 6 and 7.

## 3. Material and Methods

### 3.1 Production of nanoparticles

For the preparation of the chitosan nanoparticles (0.2 – 500nm) 250 mL of acetic acid was initially prepared at 5% concentration, then 6 g of chitosan was added to the acetic acid solution and kept under stirring for 24 hours [8].

The presence of chelating sites in the chitosan structure (Figure 8) promotes greater stability in the interactions occurring in the N and O groups, promoting an efficient anchoring due to Van der Waals interactions with the molecules of interest.



**Figure 8.** Polymer molecular structure of Chitosan.

### 3.2 Morphology of nanoparticles

The characterization of the nanoparticles by Scanning Electron Microscope (MEV), Jeol, JSM-6610, equipped with EDS, Thermo scientific NSS Spectral Imaging [9-10].

### 3.3 Anchorage of the herbicide Tebuthiuron

#### 3.3.1 Herbicide solution

The Tebuthiuron solution was prepared at the

concentration  $1 \times 10^{-4}$  mol.L<sup>-1</sup>, and 0.022835g Tebuthiuron was weighed and diluted in 1 L distilled water.

### 3.3.2 Conductometric Titration

In a 50 mL beaker where 1.0 g of chitosan was added to the Tebuthiuron solution, the mixture was acidified with 0.5 mL concentrated HCl to pH 2 with stirring for 24 h. Afterwards, the titration was started using the previously standardized 0.1 mol.L<sup>-1</sup> NaOH solution.

The titration was continued until the final solution reached pH 12, with each abrupt change in conductivity, the pH, conductivity, temperature and NaOH volume values were recorded, and at each peak an aliquot collected was collected for analysis in UV-Vis [9].

The conductometric titration procedure was carried out with control of chitosan and control with the molecule under study, for comparative purposes of displacement of spectral bands and bands of absorption.

### 3.3.3 Ultraviolet in visible region (UV-Vis)

During the conductometric titrations, the aliquots collected at the points of greatest conductivity variation were analyzed separately in the Shimadzu UV spectrophotometer UV-1800. For this analysis, 100  $\mu$ L of each conductivity peak was collected, the samples were kept at -4 °C for 48 h and after that, they were taken for analysis [10-11].

## 4. Conclusions

Through the developed analyzes it was possible to observe the performance of chitosan anchored to the herbicide Tebuthiuron.

With pH favorably adjusted, the controlled release process shows increased availability of active sites and release of ions in solution, which causes the binding charges of the chitosan structure to remain charged to promote interactions.

With these interactions, it is possible to promote an efficient anchoring due to the weak interactions with the molecule of interest

reaching the central objective of the work that is the reduction of the quantity of product used, generating a lower environmental impact.

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