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Photodegradation Kinetics of Rimsulfuron in Senegalese Surface and Groundwater, and Determination of Its Herbicidal Activity

Abdourahmane Khonté[1,2], Souleymani Ba[1], Babacar Sadikh Yatte[1], Youssoupha Diop[1], Diégane Sarr[1,2*], Diène Diégane Thiaré[2], Pape Abdoulaye Diaw[1,2], Cheikh Sall[3], Alphonse Tine[2], Atanasse Coly[2]

[1]Equipe des Matériaux, Electrochimie et Photochimie Analytique, Université Alioune Diop de Bambey, Bambey, Sénégal
[2]Laboratoire de Photochimie et d'Analyse, Université Cheikh Anta Diop de Dakar, Dakar, Sénégal
[3]Unité Mixte de Recherche d'Exploration et Diagnostic, UFR Santé, Université Iba Der Thiam de Thiès, Thiès, Sénégal
Email: *diegane.sarr@uadb.edu.sn

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Abstract

The objective of this study was to examine the photodegradation of rimsulfuron in natural waters from the Niayes agricultural zone in Senegal. This was conducted in both the presence and absence of oxalic acid, which acts as a photosensitiser. The photodegradation values of rimsulfuron in distilled water and natural waters were found to be 15.52% and 6.3% to 7.19%, respectively. The results demonstrate that rimsulfuron is relatively stable in natural waters under solar radiation in the absence of photosensitiser. The photodegradation percentage in distilled water was 68.57%, while the range in natural water was from 16.98% to 40.32%. The results clearly show that oxalic acid significantly accelerates the photodegradation of the herbicide rimsulfuron. The photodegradation reaction half-life time varies considerably, from 144.41 to 693.15 minutes, with the highest value observed in surface water (runoff water), which generally contains a greater quantity of dissolved organic matter. We then examined the herbicidal activity of the compound in question. The results of this study indicate that the herbicidal activity of rimsulfuron may be attributed to either the initial product or a combination of the initial product and its photoproduct.

Keywords

Photodegradation, Rimsulfuron, Surface and Groundwater, Photosensitizer, Herbicidal Activity

1. Introduction

Pesticides, also known as plant protection products, are substances used to control or eliminate any group of pests in order to improve crop quality and yield [1]. Following the Second World War, the application of these techniques in agriculture increased gradually and became a widespread practice. This led to a significant increase in world food production and the protection of plants throughout their development [2]. These compounds present a significant risk in natural waters, with the various processes they undergo in the aquatic environment potentially leading to their transformation into more toxic substances. While pesticides offer numerous benefits and possess unique physicochemical properties, they can also be toxic, mobile, and capable of bioaccumulation [3]. The most commonly used pesticides are fungicides, insecticides, and herbicides. Over the past four decades, these have replaced mechanical methods and have become essential to modern agriculture. Their objective is typically to eradicate weeds without affecting cultivated plants, thereby maximizing the benefits of weed elimination. This implies that different species may not react in the same manner, even within the same botanical family [4].

Herbicides represent the second most widely used class of pesticides globally, trailing only insecticides. They account for approximately 40% of all pesticides used in agricultural settings [5]. Sulfonylurea-based herbicides such as rimsulfuron are a relatively new group of compounds [6]. Rimsulfuron is a recently developed herbicide that is used for post-emergence weed control on a wide range of crops, including potatoes, maize, and tomatoes [7]. It controls several broadleaf weed species in these crops [8]. Sulfonylureas are primarily absorbed by the roots and transported by the xylem. They accumulate in the leaves, where they inhibit photosynthesis [9]. These herbicides function by inhibiting acetolactate synthase (ALS), a pivotal enzyme in the synthesis of branched-chain amino acids (isoleucine, valine) in plants [10]. Please note that exposure to natural waters may result in photodegradation of this product under the influence of solar radiation, which could give rise to photoproducts. The photodegradation of several sulfonylureas by sunlight and UV light has been the subject of extensive research in soil, water, and organic solvents. In general, photodegradation follows first-order kinetics, with the process occurring at a much faster rate during UV irradiation than during solar irradiation [11]. Scrano *et al.* studied the photolysis reactions of rimsulfuron at 25˚C by a high-pressure mercury arc (Hg-UV) and a solar simulator. Their study identified the main photoproducts following neutral and alkaline conditions as well as in acetonitrile: N-(4,6-dimethoxy-2-pyrimidinyl)-N-[(3-(ethylsulfonyl)-2-pyridinyl)]urea and N-[(3-ethylsulfonyl)-2-pyridinyl]-4,6-dimethoxy-2-pyridinamine [12].

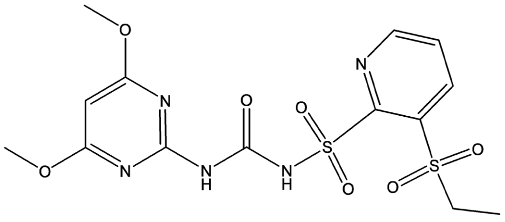
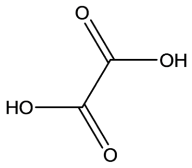
The majority of photodegradation studies on pesticides were conducted using UV irradiation sources, such as mercury lamps, a solar simulator or light-emitting diodes (LEDs) [13]-[15]. However, the use of these lamps necessitates the acquisition of costly equipment and the use of protective gear. Consequently, we conducted a study on the photodegradation of rimsulfuron under the influence of natural solar radiation. The objective of this study is to examine the photodegradation of the herbicide rimsulfuron in various natural waters in the agricultural Niayes area, Senegal. We will assess the impact of solar radiation on the herbicidal effect and determine whether the parent molecule or its photoproduct is primarily responsible for the observed results.

2. Experimental

2.1. Reagents

Rimsulfuron (98% m/m) was obtained from Sigma-Aldrich (Chemie GmbH, Eschenstrasse 5, Taufkirchen, Germany). The oxalic acid (98% m/m) was sourced from Sigma-Aldrich (PESTANAL®, analytical standard, GmbH, Switzerland). All solutions were protected against light with aluminum foil and stored in a refrigerator. The chemical properties of rimsulfuron and oxalic acid were presented in **Table 1**.

Table 1. Chemical properties of rimsulfuron and oxalic acid.

Product	Formula	Molar mass (g·mol^{-1})	WS (25˚C)[a] (g·L^{-1})	MP (˚C)[b]	BP (˚C)[c]	Structure
Rimsulfuron	$C_{14}H_{17}N_5O_7S_2$	431.44	7.3	172 - 178	Decomposes before boiling	
Oxalic acid	$C_2H_2O_4$	90.03	118	189 - 191	365.8	

[a]Water solubility (25˚C), [b]Melting point, [c]Bolting point.

2.2. Materials

Absorption spectra were measured using a GENESYS™ 180 UV-Vis Spectrophotometer with the following specifications: Wavelength Range: 190 nm to 1100 nm, Scanning speed: Slow, medium and fast (up to 1600 nm/min), Spectral bandwidth: 2 nm. The PULMIC brand (France) provided the Raptor 16 L sprayer for use. Solar measurements were taken using a Tenmars TM-207 BTU Solar Power Meter with remote sensor/Pyranometer (Taiwan region), with a power of 2000 W/m^2. A thermometer and pipette were used to measure temperature. A 50 - 1000 μL micropipette (Gilson, France) was used for dilution.

2.3. Procedure

2.3.1. Solution Preparation

All standard solutions of rimsulfuron (10^{-3} M) and oxalic acid (10^{-3} - 10^{-1} M) were freshly prepared in distilled water. The requisite working standard solutions were prepared by taking the appropriate quantity from the stock standard solutions. To prevent any decomposition, all solutions were protected from light with aluminium foil and stored in a refrigerator.

The distilled water was prepared at the Iba Der Thiam University in Thiès, Senegal.

2.3.2. Preparation of Water Samples

Natural water samples from the Niayes agricultural area of Senegal were collected in 1.5 L glass bottles in accordance with standard procedure. The samples were filtered using a syringe filter with a PTFE membrane with a diameter of 25 mm and a pore size of 0.2 μm (Sigma-Aldrich), in order to remove any suspended organic matter.

2.3.3. Determination of Herbicidal Activity

To ascertain the herbicidal efficacy of the product, two 2 m^2 grass plots were established on clay soil. One of the plots is exposed to sunlight with an average energy of 1270 W/m^2, while the other is protected from light. We followed the evolution of the weeds for 18 days.

On each plot, we spray the grass with a pesticide solution in accordance with the instructions on the pesticide bottle (0.5 L per hectare).

Therefore, 500 mL of rimsulfuron must be used per hectare, which corresponds to an application volume of 0.2 mL of rimsulfuron per 4 m^2. Additionally, for 25 mL of rimsulfuron, the product must be diluted in 15 L of water. To maintain the same concentration and ensure that all the grass is sprayed, 10 mL of rimsulfuron should be added to 6 L of water. The following protocol was followed: First, 1 L of water was added to the sprayer, followed by 10 mL of rimsulfuron. The solution was stirred thoroughly to ensure uniform distribution. Finally, the remaining 5 L of water was added while stirring the solution.

Following the application of the spray, each plant is watered daily. Subsequently, the impact of our irradiated and non-irradiated products on the herbs is assessed every two days until day 18.

3. Results and Discussion

3.1. Photodegradation Study of Rimsulfuron

Figure 1 presents the electronic absorption spectra of rimsulfuron in distilled water and natural water samples (well waters and runoff water) in the absence of the photosensitiser at different irradiation times (t_{irr} = 0 to 120 min). In all cases, the spectra of the irradiated and non-irradiated products show a maximum band at 375 nm. This intense band is attributed to the delocalisation of the π electrons.

This value is in good agreement with the results of the literature on the maximum absorption wavelength of sulfonylurea pesticides [15].

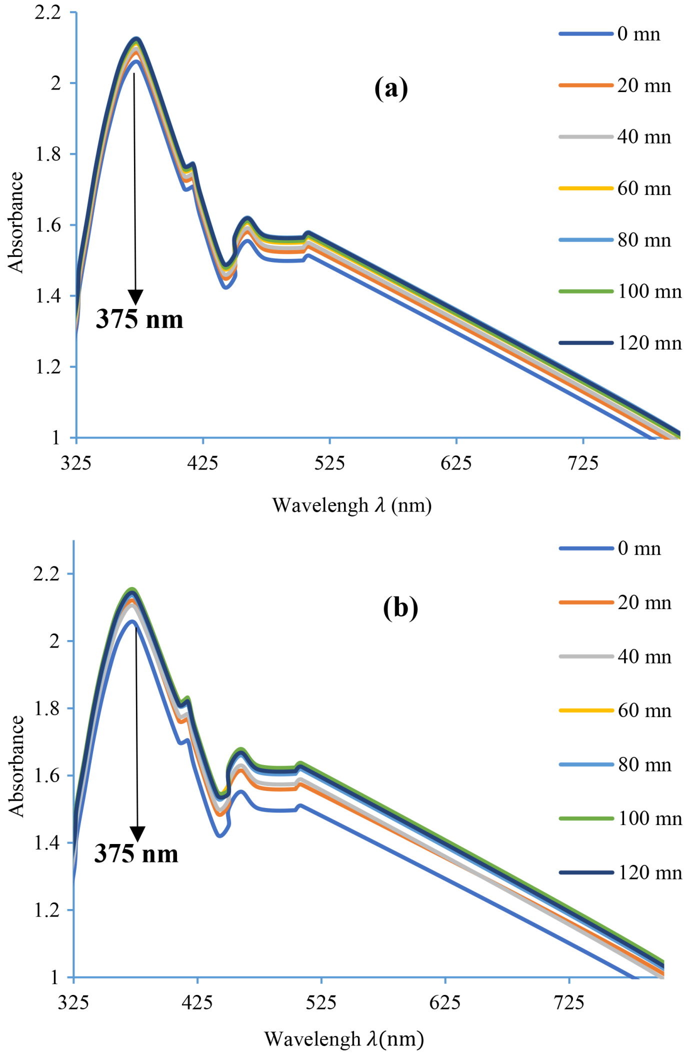


Figure 1. Evolution of the absorption spectra of rimsulfuron (10^{-4} M) in the absence of a photosensitiser in well water (depth = 0.5 m) (a) and in runoff water (b) during irradiation time.

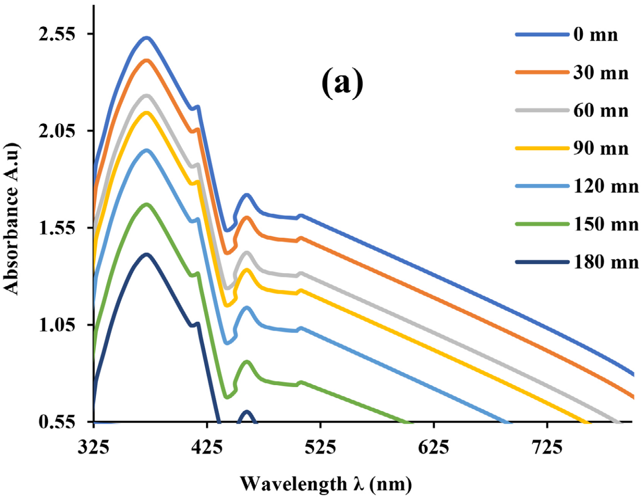
During the irradiation process, we noted a slight variation in absorbance as a function of irradiation time. Accordingly, the quantity of rimsulfuron transformed into a photoproduct or the percentage of photodegradation over the course of 120 minutes was determined using the following equation: $\left(\frac{A_0 - A}{A_0}\right)\times 100$. In this calculation, A represents the absorbance at $t_{\text{irr}} = 120$ minutes, while A_0 represents the absorbance at $t_{\text{irr}} = 0$.

The results clearly show that the photodegradation percentages in distilled water are 15.52%, while those in natural water samples are significantly lower (between 6.3% and 7.19%). The photodegradation percentage of rimsulfuron in distilled water is approximately twice that observed in water samples. The discrepancy can be attributed to the lack of ions and organic matter present in distilled water. As has been documented in numerous studies, the presence of organic matter frequently serves to reduce the rate of photodegradation of pesticides. We can cite the work of Sambou *et al.* on the photodegradation of the herbicide diuron by photochemically induced fluorescence (PIF) as an illustrative example [16]. As well as those of Saleck *et al.* on the photodegradation of diuron and metalaxyl by UV-visible and PIF [17].

To enhance the photodegradation of rimsulfuron in water, we noticed that the use of a photosensitiser would be an effective method to accelerate the photodegradation process. To achieve this objective, we conducted photodegradation experiments with the herbicide in distilled water and natural waters using oxalic acid as a photosensitiser.

3.2. Photodegradation Study of Rimsulfuron in the Presence of a Photosensitizer

This section presents the results of the study on the photodegradation of rimsulfuron in distilled water and in natural water samples in the presence of the photosensitiser during an irradiation time of 180 min. Initially, we optimised the concentration of oxalic acid in the range of 10^{-4} M to 2×10^{-1} M and found an effect of oxalic acid on the photodegradation of rimsulfuron at concentrations above 10^{-2} M. At the above concentrations, a significant effect of oxalic acid on the photodegradation of the herbicide was observed, and the optimal concentration was determined to be 10^{-1} M. Subsequently, the concentration of oxalic acid was set at 10^{-1} M to study the photodegradation kinetics of the herbicide rimsulfuron in distilled and natural water. Thus, we present in **Figure 2** the evolution of the absorption spectra in the presence of oxalic acid (10^{-1} M) in well water (depth = 0.5) and runoff water. As the rimsulfuron solution is irradiated in the presence of oxalic acid (10^{-1} M), a decrease in absorbance was observed; this indicates degradation of the rimsulfuron.



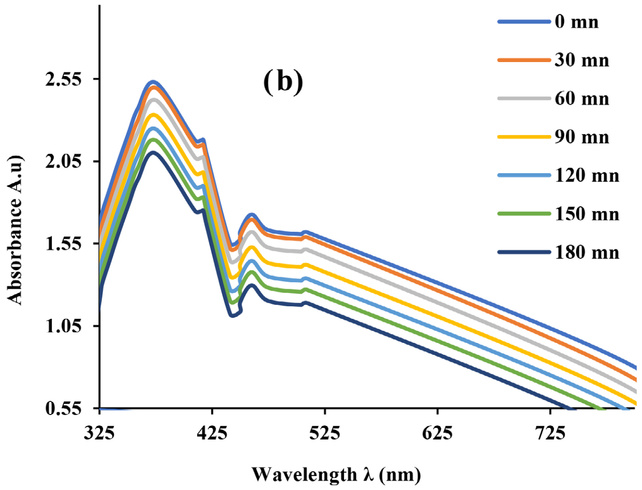


Figure 2. Evolution of the absorption spectra of rimsulfuron (10^{-4} M) in the presence of a photosensitiser in well water (depth = 0.5 m) (a) and in runoff water (b) during irradiation time.

This reduction appears to be greater in distilled water and well water (depth = 0.5) than in well water (depth = 1 m) and runoff water. However, our findings indicated that the photodegradation of the herbicide in the presence of the photosensitiser was significantly enhanced. The photodegradation percentage was 68.57% in distilled water, 40.32% in well water (0.5 m), 20.71% in well water (1 m), and 16.98% in runoff water. The discrepancy in photodegradation rates may be attributed to the considerable organic matter and ion content in the water samples. The pH of water samples had no significant impact on rimsulfuron photodegradation. However, we found that the percentage of photodegradation decreases as a function of the conductivity of the water sample. The highest conductivity measurement recorded (35.15 mS/cm) in runoff water is likely responsible for the low photodegradation percentage observed (Table 2). This suggests that the presence of ions in the samples contributes to the herbicide's persistence in natural waters. The results clearly show that rimsulfuron is susceptible to solar radiation when a photosensitiser is present. To gain a deeper insight into the stability of our product in natural waters, it is crucial to examine the parameters of photodegradation kinetics, specifically the photodegradation rate constant and photodegradation reaction half-life time. To evaluate the photodegradation kinetics of the herbicide in various distilled water and natural water samples, we determined that the photodegradation kinetics of rimsulfuron is of the first order. For the first-order reactions, the following equations were used:

$$\ln\frac{A_0}{A} = kt$$

$$t_{1/2} = \frac{\ln 2}{k}$$

with k the photodegradation rate constant and $t_{1/2}$ the photodegradation reaction half-life time.

The resulting curves $\ln\frac{A_0}{A} = f(t)$ yield a straight line with a correlation coefficient close to unity, indicating first-order kinetics (**Figure 3**). The rate constants and half-lives were determined from the slopes obtained. The kinetic parameters were presented in **Table 2**.

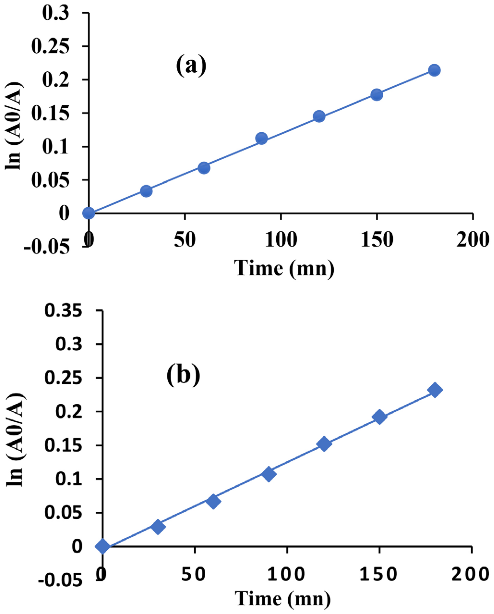


Figure 3. First-order kinetic of rimsulfuron in the presence of photosensitiser in well water (depth = 0.5 m) (a) and runoff water (b).

Table 2. Kinetic parameters for the photodegradation of rimsulfuron in the presence of photosensitizer.

Matrix	k (min^{-1})^{a}	Order^{c}	$t_{1/2}$ (mn)^{b}	PP^{d} (%)	$r^{2\ e}$	pH	σ (mS/cm)^{f}
Distilled water	$(4.80 \pm 0.2) \times 10^{-3}$	1	144.41	68.57	0.998	7.02	0.07
Well water 0.5 m	$(2.9 \pm 0.3) \times 10^{-3}$	1	239.00	40.32	0.996	8.10	2.95
Well water 1 m	$(1.3 \pm 0.2) \times 10^{-3}$	1	533.20	20.71	0.997	7.80	3.64
Runoff water	$(1.0 \pm 0.1) \times 10^{-3}$	1	693.15	16.98	0.990	7.6	35.15

[a] k = photodegradation rate constant (min^{-1}) and absolute error (±). [b] $t_{1/2}$ = photodegradation reaction half-life time (min). [c] Order = reaction kinetic order. [d] Photodegradation percentage. [e] r^2 = kinetic equation correlation coefficient. [f] Conductivity of the water samples.

We found that in the presence of photosensitiser, the rate of photodegradation of rimsulfuron is lower in runoff water ($t_{1/2}$ = 693.15) under the effect of solar radiation. This suggests that there is a high likelihood of this product being transported in runoff water. This result is in line with the findings of Allan J. Cessna *et al.* [18], who studied the persistence of three herbicides, including rimsulfuron, in ponds. However, in the presence of oxalic acid, this product is susceptible to degradation in these waters under the influence of solar radiation. Thiaré *et al.* also observed similar kinetics when studying the photodegradation of fenvalerate, a pyrethroid insecticide, in water using a solar simulator [19]. Another study by Scrano and collaborators demonstrated that all chemical and photochemical processes responsible for the disappearance of rimsulfuron followed second-order kinetics [14]. Other researchers, such as Vicari *et al.* have obtained first-order kinetics for this herbicide by studying its degradation in sandy-loamy soil [20]. Sarr *et al.* conducted studies on the photodegradation of fluometuron. Their findings indicated that the photodegradation reactions of this product follow first-order kinetics [21].

3.3. Herbicidal Activity of Rimsulfuron

The objective of this study was to assess the herbicidal activity of rimsulfuron. Following application of rimsulfuron solution to exposed, sun-protected grasses over an eighteen-day period (**Figure 4**). From the fourth day onwards, the herbicidal effect on leaves kept away from light was found to be less significant (**Figure 4(b)**). The herbicidal efficacy of the treatment remained constant on sun-protected grasses until day 18 (**Figure 4(b)**, **Figure 4(c)** and **Figure 4(d)**).

However, a noticeable change in impact was observed on light-exposed grasses. The majority of light-exposed grasses were desiccated by day eight, and all specimens showed near-total mortality by day eighteen (**Figure 4(d)**).

The results indicate that the herbicidal activity of rimsulfuron can be attributed to either its photoproduct or its combined action with its photoproduct.

Wei *et al.* achieved comparable outcomes through an investigation into the herbicidal efficacy of three pesticides belonging to the same chemical family as rimsulfuron, along with their degradation products, on green algae. The results demonstrated that the parent products exhibited greater herbicidal activity. The ineffectiveness of the degradation products on these algae was due to the fact that the nitrogen in these products was used by the algae as an energy source, thereby reducing their toxicity [22]. The results of our study, when compared with those of Wei *et al.*, demonstrate that the herbicidal activity of a compound or its degradation product may be contingent on not only the nature of the plant under study, but also on the sources of degradation, which may result in the formation of different products.

(a)

(b)

(c)

(d)

Figure 4. (a) Grass condition on the first day of rimsulfuron application; (b) Grass condition on the fourth day of applying rimsulfuron; (c) Grass condition on day 12 after rimsulfuron application; (d) Grass condition on day 18 of rimsulfuron application.

4. Conclusions

The results of this study demonstrate that rimsulfuron is stable in natural waters when exposed to solar radiation. However, it should be noted that the chemical is unstable in the presence of oxalic acid, which acts as a photosensitiser. As a result, there is a greater likelihood of contamination of surface water than groundwater at low infiltration rates.

Studies on herbicidal activity have demonstrated that it is more effective in the presence of light. Given the slow degradation of this product under the influence of solar radiation, it is possible that the herbicidal activity is due either to the photoproduct alone, or to the combined action of rimsulfuron and its photoproduct. The results of this study will provide a reliable basis for monitoring the photodegradation of herbicides used in the Niayes agricultural zone in Senegal. Furthermore, the results will facilitate the safe use of herbicides in environmental matrices. The objective is to guarantee the optimal use of pesticides by farmers, who are frequently unaware of the impact of solar radiation on these substances. This will ensure the best possible health and safety conditions.

Authors' Contributions

Khonté, A. drafted the original manuscript and analysed and interpreted the results. BA, S., is a PhD student. He carried out the sampling and participated in the work. Yatte, B.S. is a PhD student. He participated in the work. Diop, Y. is a PhD student. He also participated in the following projects. Sarr, D. was involved in the design, analysis and interpretation of the study results. Thiaré, D.D., participated in the analysis and interpretation of the results. Diaw, P. A. made critical corrections to the manuscript. Sall, C. participated in the experimental protocol and carried out the work in his laboratory. Tine, A. contributed to the design of the study. Coly, A. is the main supervisor of this work.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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