Nature Environment and Pollution Technology
An International Quarterly Scientific Journal
p-ISSN: 0972-6268 (Print copies up to 2016)
e-ISSN: 2395-3454
Vol. 20 No. 2 pp.533-539 2021
Original Research Paper
https://doi.org/10.46488/NEPT.2021.v20i02.009
Open Access Journal

Study of the Insecticidal Potential of Diatomaceous Earth from Sig (Algeria) on the *Dermestes haemorrhoidalis* - A Pest of Stored Food Products

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 20-04-2020
Revised: 20-05-2020
Accepted: 25-06-2020

Key Words:
Dermestes haemorrhoidalis
Diatomaceous earth
Insecticidal activity
Natural insecticide

ABSTRACT

The insecticidal activity of the Diatomaceous Earth (DE) of Sig was assessed against the *Dermestes haemorrhoidalis*, which is the main pest affecting wheat stored in Blida, a central region of Algeria and one of the four cereal regions managed by the Algerian Inter-branch Cereals Office (AICO). The formulation was tested at two different doses: 500 and 1000 ppm against adults of the species. The bioassays were carried out in 1-litre glass jars containing soft wheat with an average moisture content of 60% mixed with diatomaceous earth and maintained at 27°C and 70% of humidity. The effectiveness of the treatment was assessed by recording adult mortality after 2, 7 and 14 days. Sig's diatomite showed significant insecticidal activity against *Dermestes haemorrhoidalis* after only two days of treatment with both doses 500 and 1000 ppm. After 14 days, average mortality was more than 95% even at 500 ppm. Furthermore, electron microscopy of the diatomite particle from Sig (Algeria) reveals the architecture of the frustule. It shows a porous and brittle siliceous shell made largely of diatomite "skeletons". This research work allowed getting insights into the mechanism of action of diatomite on the *Dermestes haemorrhoidalis*. On the other hand, the identification of diatomite of Sig was performed by X-ray diffraction and infrared.

INTRODUCTION

Chemical pesticides are widely used around the world. Their negative impact on animal and plant health has been widely highlighted in the literature (Testud & Grillet 2007, Hazarika 2011, Ghorab & Khalil 2016, Richardson et al. 2019). Metabolites from carbamates and phosphines, which are toxic substances, persist in nature in large quantities (Meiniel 1977, Steeve 2013, Lotti & Moritto 2005, Martin-Reina et al. 2017). The control of insects that destroy stored food still relies on chemicals, but following the growing concerns regarding the issue, a renewed interest in Diatomaceous Earth (DE) has been shown in recent years in the field of applied sciences (Ebadollahi & Sadeghi 2018, Athanassiou et al. 2016). This is particularly the case for the disinfection of premises and protection of stored food (Banks & Fields 1995, Bridgeman 1998, Desmarchelier et al. 1992, Korunić et al. 2016). Indeed, DE has long been used to protect the stored grain. These fossils give, after extraction, crushing and grinding, a fine powder primarily composed of amorphous silicon dioxide (SiO_2) with a small amount of aluminium, iron, magnesium, CaO and sodium oxide. The highly porous, inert and sharp architecture of the frustules of the DE is used for its abrasive and desiccating properties (Quarles & Winn 1996, Korunić et al. 2016).

The insecticidal activity of DE is essentially attributed to dehydration of the insect provoked by damage to the cuticle layers of the integument. The DE particles are trapped on the insect's body and absorb lipids in the waxy layer of the epicuticle causing degradation of the exoskeleton (Ebeling 1971, Korunić et al. 2016, Mewis & Ulrichs 2001).

However, insecticidal efficiency depends significantly upon the physical, chemical and morphological characteristics of the diatomite species in DE (Korunić et al. 2016, Rojht et al. 2010) and particle size (Korunić 2013, Subramanyam & Roesli 2000). It also depends upon the resistance of the host insects (Aoues et al. 2017).

The use of DE to control food pests offers a number of advantages: it does not leave chemical residues, has low toxicity, is inexpensive and can be easily disposed (Korunić et al. 2016). DE has been used to treat wheat contaminated with C. ferrugineus. It has also been used for the elimination of *Sitophilus oryzae* and red flour beetle *Tribolium castaneum*

Herbst from rice and wheat (Korunic et al. 2016).

The objective of this paper is to describe the physico-chemical analysis of Sig's DE and to carry out a preliminary test regarding pest control potential on food pests under natural storage conditions in the hot and humid region of Blida, Algeria.

MATERIALS AND METHODS

Preparation of the Samples

The diatomite used in this work is a raw Algerian white diatomite from the National Company of Mining Products Non-Ferrous and Useful Substances (ENOF) deposit located at 5 Kms from southeast of the city of Sig in the Wilaya (province) of Mascara, hereafter referred to as diatomite of Sig (DTS). The collected diatomite samples were crushed and dried, ground as finely as possible and sieved to a particle size less than 63 µm. The obtained products were subject to physicochemical, spectroscopic and structural characterization, and used in all the experiments.

White grains used in the experiments were first sieved to remove impurities and then stored hermetically in glass jars at room temperature.

An experimental unit consisted of a glass jar containing 1 kg of soft wheat, to which DTS powder was added and then carefully hand-mixed. Fifty (50) adult insects (*Dermestes haemorrhoidalis*), *Dermestidae* family and **Beetles** order, 2 weeks old on average, was introduced into the jar. The same procedure was followed for each concentration of DTS with an interval of 2, 7 and 14 days of exposure.

An additional jar containing untreated wheat was used (as control sample) for each series of tests. Three treated samples: 500 ppm, 1000 ppm and control (untreated) were used for each time interval. After 2, 7 and 14 days of exposure, the contents of the jars were screened, living and dead insects were collected and counted. Mortality is expressed as a percentage of adult deaths out of the total number of beetles found in each jar. The experiments were carried out from May to July 2019.

The *Dermestes haemorrhoidalis* adults used for the experiments were obtained from a wheat stock in the region of Blida. The insects were kept under the same infestation conditions at a temperature of 25 ± 1 °C and relative humidity (RH) of %60 on average. Identification of the pest was carried out using a key developed by Oleobel and Tran, (1993). The species are stored food beetles: black beetle of the pantry (*Dermestes haemorrhoidalis*) (Fig. 1).

Characterization of DTS

The X-ray diffraction (XRD) analysis of the DTS powder was carried out using a BRUKER D8 ADVANCE Eco,

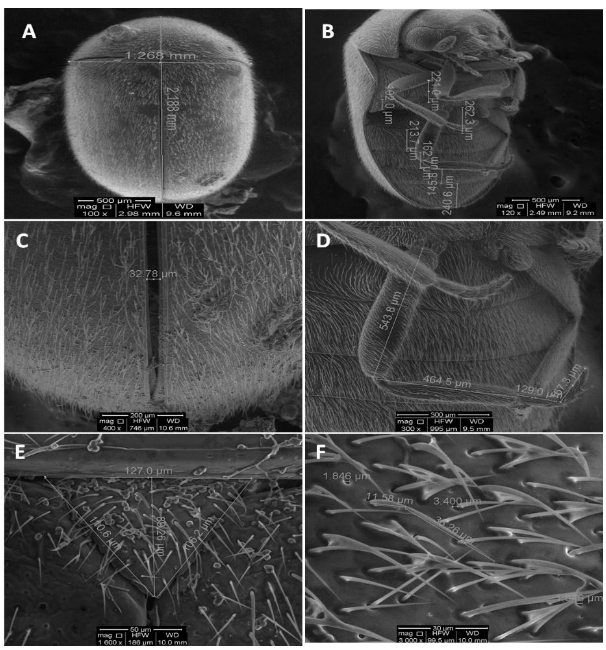

Fig. 1: SEM observation of untreated *Dermestes haemorrhoidalis*, A, C and E: dorsal side, B and D: ventral side, F: Dorsolateral face showing cuticular thoracic depressions surrounding the sensory bristles.

equipped with a Cu anticathode (λ = 1.5418 Å) generating a power of 40 mA, 45 KV and mode 2 THETA, scanning area [3.0001- 89.999482°], a step of 0.020171°, time per step: 0.5 s. Software for the acquisition and processing of data are respectively: Data Collector and High Score Plus of PANalytical.

To study the thermal properties of DTS, samples of (2 mg) were measured using the SeikoSSC5200 thermal analyser (model 220 TG/DTA) at heating and flow rates of 10-50°C/min and 100 mL/min, respectively. Analysis and data processing software are TA Instrument Explorer and TA Universal Analysis, respectively.

DTS grain scanning electron microscopy was performed with a Quanta 250 from FEI and a tungsten filament as an electron source.

The infrared absorption spectra were plotted with a BRUKER Alpha type device; the analysis was done in ATR mode with a resolution of 2 cm^{-1} for 24 scans.

The elementary analysis of DTS was carried out with Rigaku ZSX Primus II X-ray Fluorescence Spectrometer, elementary coverage: ^{4}Be à ^{92}U. Closing window, Rh-anode, 3 kW or 4 kW, 60 kV. Primary X-ray filter: Al25, Al125, Ni40 and Ni400. Heavy Element Detector: Scintillation Counter (SC).

The volumetric distribution of DTS was assessed by laser granulometry using MALVERN MATERSIZER 2000 granulometer equipped with Scirocco as a dry dispersion accessory; sensitivity normal, absorption 0.1 and obscuration 5,68%.

Statistical Analysis

ANOVA was used to evaluate the treatment and exposure time of DTS on mortality of *Dermestes haemorrhoidalis*. The results are presented as mortality percentage of *Dermestes haemorrhoidalis* at 500 ppm and 1000 ppm of DTS, respectively and the exposure time of 2, 7 and 14 days respectively.

RESULTS AND DISCUSSION

Phase quantification of DTS by XRD analysis was conducted using MAUD software as illustrated in Fig. 2. DTS powder consists of amorphous and crystalline phases. The main constituents of crystalline phases are $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3 on the MAUD database records. The results agree with the result obtained by Pokorný et al. (2017).

The SEM of DTS (Fig. 3) shows the pores and the cylindrical and/or disc form of this powder. The average size of the diatomite particles determined by laser granulometry

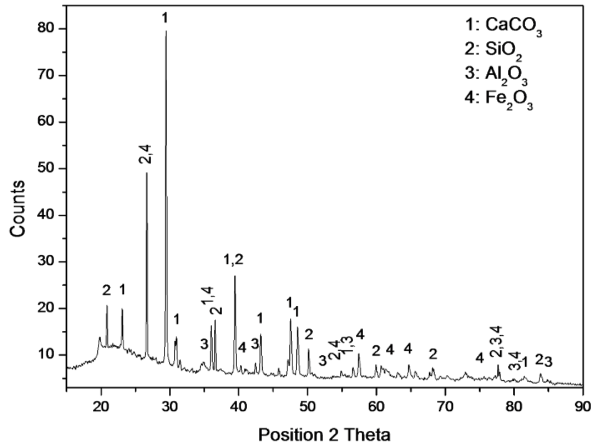

Fig. 2: X- ray diffraction pattern of diatomite of Sig (DTS).

is ~ 12 µm (Fig. 4), with a specific surface area of 1.61 m^2/g. the average particle diameter is in the range 3,802 - 34,674 µm; similar results were obtained by Fragoulis et al. (2005) where they found a diameter < 30 µm.

The elemental composition of DTS was obtained by X-ray Fluorescence (XRF); the fire loss is 7.4% and the moisture content is 2.5%. Results of the chemical analysis of the material (Table 1) show that the diatomite is largely made up of silica, CaO and aluminium oxide. Other elements are present but in much smaller amounts.

Fourier Transform Infrared Spectroscopy (FTIR) analysis of DTS (Fig. 5) shows the main absorption bands of our untreated diatomite are in agreement with the literature (Yuan et al. 2004, Caliskan et al. 2011). Indeed, the wide band in the wave number range 3100 - 3500 cm^{-1} characterizes the vibration of the OH group of water contained in the DTS, as well as the Si-OH group, which are observed at 3690 and 3614 cm^{-1}, OH and Si-OH, respectively. The weak vibration at 3600 cm^{-1} indicates the presence of unbound water, i.e. free OH. On the other hand, water deformation appears at 1640 cm^{-1} (Yuan et al. 2004) while vibrations centred at 1440, 875 and 712 cm^{-1} indicate CO_2 deformation (Yuan et al. 2004, Caliskan et al. 2011). The characteristic peaks of the skeleton (Si - O - Si) are located at 1073 and 997 cm^{-1} (Caliskan et al. 2011). The band centred at 874 cm^{-1} corresponds to the elongation vibration of the silanol group (Si-O). The peaks at 798 and 713 cm^{-1} are due to Si-O-H vibrations. The absorption peak around 570 cm^{-1} can be assigned to the deformation vibration of the entity Si-O-Si. The intense band at 460 cm^{-1} is relative to the angular vibration of (Si - O - Al) and /or (Si - O - Si) (Caliskan et al. 2011).

Results of the simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis of the DTS are shown in Fig. 6. The evolution of diatomite in

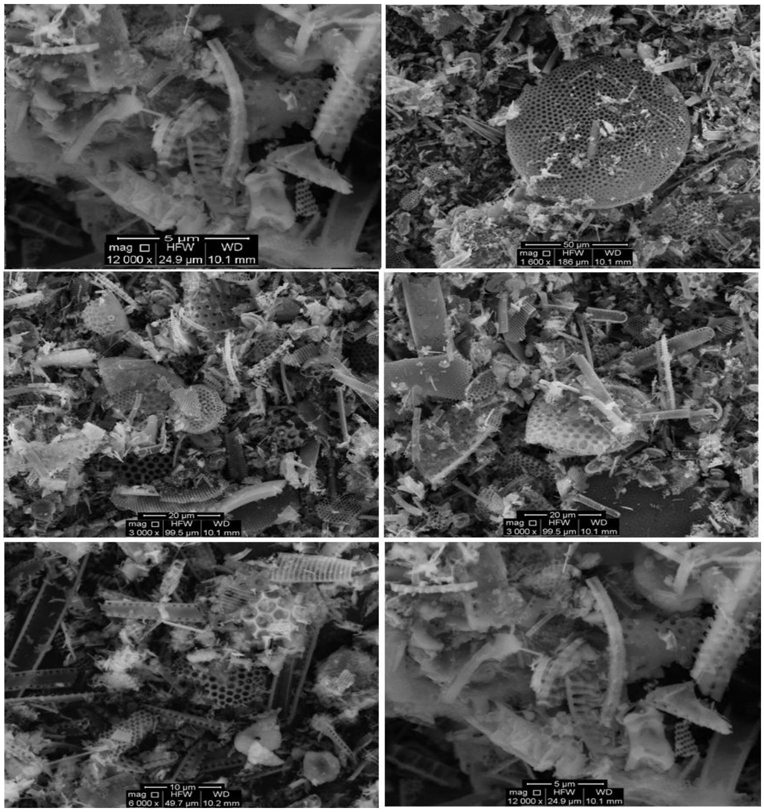

Fig. 3: SEM observation of the diatomite of Sig (DTS) at different magnifications.

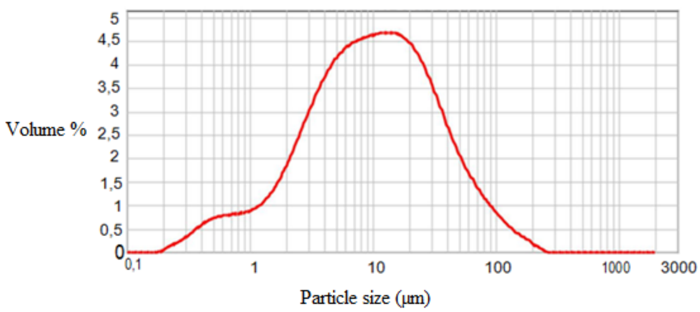

Fig. 4: Particle size distribution of diatomite of Sig (DTS).

Table 1: Chemical composition of diatomite of Sig.

Constituent and weight %									
CO_2	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2
9.40	0.26	1.27	3.87	64.08	0.16	0.08	0.89	17.64	0.26
Constituent and weight %									
MnO	Fe_2O_3	NiO	ZnO	Rb_2O	SrO	ZrO_2	Cl		
0.01	1.77	0.01	0.01	0.01	0.05	0.01	0.15		

the TGA agrees well with the literature (Meradi et al. 2015, Mendioroz et al. 1989). The DTS placed on the balance at 15°C with a step of 10°C/min. The spectrum (Fig. 6 A) shows a mass loss of 3.31% between 100 and 200°C; water

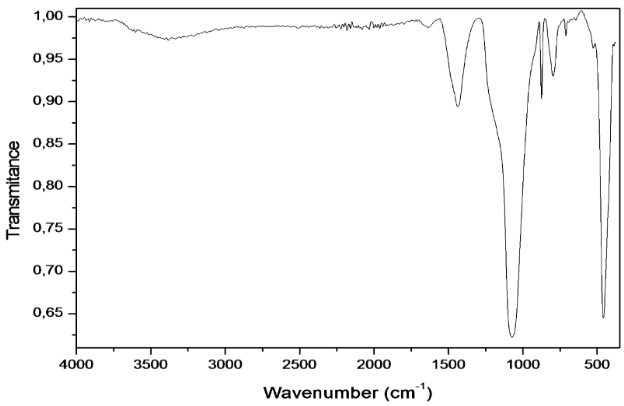

Fig. 5: Fourier Transform Infrared Spectroscopy spectra of diatomite of Sig (DTS).

vapours that escape, represent humidity. The mass loss of 16% between 300 and 700°C corresponds to the decomposition of the organic material and the dehydroxylation of the silanol group. The organic material results primarily from the impurity content of the deposit produced by chemical precipitation, atmospheric contact and environmental conditions, as well as from amorphous silica, the main constituent of diatomite. Metal oxides, clays, carbonates may also be present (Mendioroz et al. 1989). The literature also reports the phenomenon attributed to the dehydroxylation of calcium hydroxide (Benkacem et al. 2016).

As can be seen from the DST results (Fig. 6 B), the first endothermic peak at 106.45°C corresponds to water desorption whereas the second, at 689.07°C, corresponds to the dehydroxylation (Meradi et al. 2015, Mendioroz et al. 1989).

The SEM Examination of the cuticular surfaces of the *Dermestes haemorrhoidalis* treated with DTS reveals that the dorsal cuticle is evenly covered with fragments of the diatomite frustule on the integumentary surface (Fig. 7).

Table 2 shows the percent mortality of *Dermestes haemorrhoidalis* at 500 and 1000 ppm of DTS following exposure for 3different periods of time (2, 7 and 14 days).

The mortality of *Dermestes haemorrhoidalis* is in agreement with results obtained by Ebeling (1971) and Golob (1997). Indeed, a concentration of 1000 ppm generated mortality of 56.0±1.15% after 2 days, 78.7±0.67% after 7 days and 90.7±0.67% within14 days, and is higher than the result obtained with 500 ppm with 50.7±0.67% after 2 days, 56.7±4.37% after 7 days and 80.7±0.67% after 14 days.

Table 3: Shows that treatment and exposure time of *Dermestes haemorrhoidalis* by DTS gives a very significant correlation ($P \leq 0.001$).

Complete pest annihilation was not observed for two reasons:

1. The high RH (60% on average) caused saturation of the DTS and allowed the insect to recover any water loss.
2. In general, diatomite exhibits an activity consistent with its chemical constitution (Athanassiou et al. 2005)**.**

The diatomite of the regions of Sig Algeria, with 90% efficacy against *Dermestes haemorrhoidalis* and many other nuisances, can be considered as an appreciable natural insecticide material. Indeed, this non-metallic material offers the sought-after advantage of being, available, low cost, and -biocompatible. It also possesses excellent physicochemical properties such as non-toxicity, lightness, unique structure of the pores, porosity, excellent absorption capacity, chemical inertness and large available reserves (Sun et al. 2013).

Diatomite is an economical and beneficial solution for human, animal and plant health.

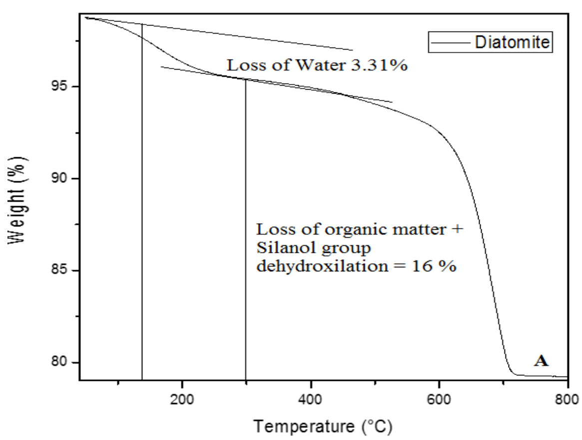

Fig. 6. A: Thermogravimetric Analysis (TGA) of diatomite of Sig (DTS).

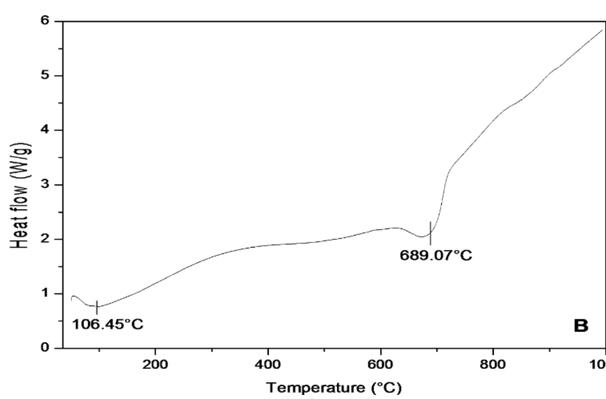

Fig. 6. B: Differential Scanning Calorimetry (DSC) analysis of diatomite of Sig (DTS).

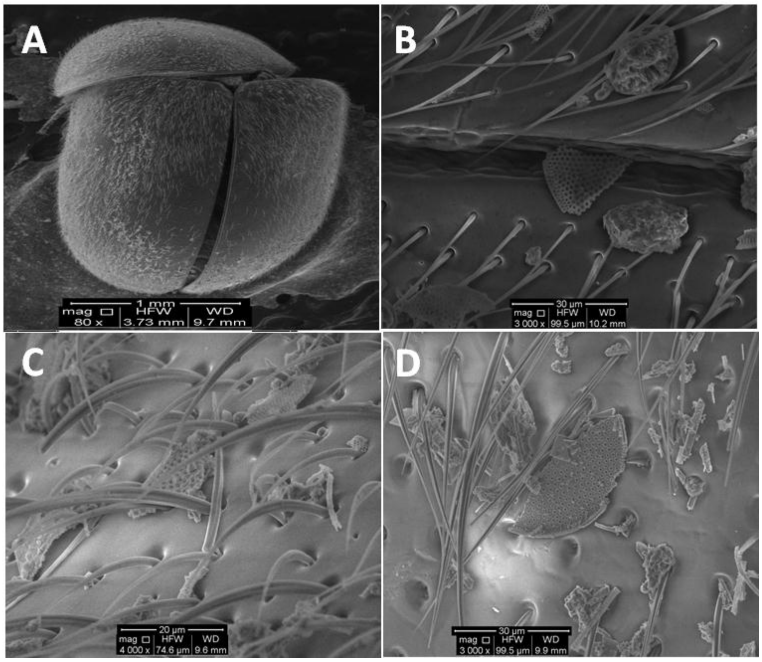

Fig. 7: SEM images of *Dermestes haemorrhoidalis* treated with diatomite of Sig (DTS) particles, A: dorsal side, B: Fragments of siliceous frustule in the dorsal fringe of the insect, C and D: Cuticular sites on the dorsal surface surrounding sensory bristles contaminated with DTS.

Table 2: Mean (±SE) percent mortality of *Dermestes haemorrhoidalis* when exposed to diatomite of Sig (DTS) for 2, 7 and 14 days.

Duration of exposure (days)	Treatment (ppm of DTS)		F_{df}, P
	500	1000	
	Mortality of *Dermestes haemorrhoidalis*		
2	50.7±0.67%	56.0±1.15%	$15.7_{1,4}$, 0.02
7	56.7±4.37%	78.7±0.67%	$31.7_{1,4}$, 0.005
14	80.7±0.67%	90.7±0.67%	$100.1_{1,4}$, <0.001

Table 3: ANOVA table showing the significance of treatment and exposure time on mortality of *Dermestes haemorrhoidalis*.

Variable_{df}	F, *P*
$\text{Treatment}_{1,12}$	90.12, < 0.0001
$\text{Exposure}_{2,12}$	195.19, < 0.0001
$\text{Treatment*Exposure}_{2,12}$	12.21, 0.001

CONCLUSION

The study confirms the natural pest control property of the diatomite from Sig (Algeria). The DTS gives satisfactory results with a mortality rate of 90% within 14 days on *Dermestes haemorrhoidalis,* the main pest of wheat in the region of Blida (Algeria). Physicochemical characterisation shows that, by its particular structure, morphology and texture, our diatomite is naturally endowed to control the pest. This siliceous material is an active structure on the cuticle of the *Dermestes haemorrhoidalis.* Scanning Electron Microscopy reveals the dispersion and absorbance properties of the diatomite on the cuticle. It also shows the abrasive and lacerating effects of the diatomaceous earth. This control capacity on *Dermestes haemorrhoidalis* populations highlights the ecological advantage of the diatomite from Sig.

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