UNIVERSIDAD AUTÓNOMA AGRARIA ANTONIO NARRO

SUBDIRECCIÓN DE POSTGRADO

RESPUESTAS DE TOMATE (*Solanum lycopersicum*) A LA APLICACIÓN DE NANOPARTICULAS DE ZnO Y TiO_2

Tesis

Que presenta ENEIDA ADILENE PÉREZ VELASCO

como requisito parcial para obtener el Grado de

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Elaborada por ENEIDA ADILENE PÉREZ VELASCO como requisito parcial para obtener el Grado de Doctor en Ciencias en Agricultura Protegida con la supervisión y aprobación del Comité de Asesoría

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MORPHOLOGY, SURFACE MODIFICATION AND APPLICATION FORM OF ZnO NANOPARTICLES AFFECT GROWTH, YIELD, GAS EXCHANGE PARAMETERS AND NUTRIENT STATUS IN TOMATO

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Abstract:	Nanotechnology is contributing to transform the conventional agriculture. Nanoparticles (NPs) of ZnO are reported to enhance plant growth, however, during the syntheses, NPs tend to agglomerate, affecting their dispersion. Agglomeration can be counteracted if NPs surface is modified, resulting in improved dispersion and stability. The morphology of NPs also affects their stability, and physical and chemical properties. In the present study, the surface of spherical or hexagonal NPs-ZnO was modified with maltodextrine (MDX) and either foliar or drench applied at 1500 ppm in soilless cultivated tomato. Hexagonal and spherical NPs increased plant growth, yield, fruit quality, fruit nutrient status and gas exchange parameters. Fruit P, K, Ca, Mg, Mn and Si concentration was higher in plants treated with hexagonal NPs-ZnO modified with MDX and applied by drench; however, Zn was higher when spherical or hexagonal no surface modified NPs were applied by either foliar sprays or drench. Significant but marginal increases in plant growth and yield were obtained by drench applications compared to foliar sprays. In general, spherical or hexagonal NPs produced similar results. Despite the yield increase, the morphology of the NPs, alone or combined with foliar or drench applications did not affect fruit yield or quality. MDX applied alone increased fruit yield and quality, although when combined with NPs morphology did not result in growth and yield improvement.	
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ÍNDICE

INTRODUCCIÓN

Frente al aumento poblacional del mundo se encuentran diversos obstáculos para la producción de alimentos, los cuales deben mantenerse al día para lograr cubrir las necesidades de los consumidores. Existen diversos desafíos que deben superarse para la producción alimenticia como las sequías, problemas ambientales, cambio climático (Cheng *et al.,* 2016) y sobre todo el uso excesivo de fertilizantes minerales que ocasionan contaminación y problemas en la salud humana. La agricultura es un área en donde comúnmente se aplican tecnologías nuevas para mejorar la calidad, rendimiento de los cultivos y también para aumentar la capacidad de tolerancia de las plantas ante factores bióticos y abióticos (Srilatha, 2011). La nanotecnología emerge como un avance tecno-científico que desarrolla y aplica herramientas (nanomateriales) que ayudan a detectar con mayor rapidez enfermedades fitopatógenas así como aumentar la capacidad de las plantas para la absorción de agua y nutrientes y además eficientar el uso de pesticidas (Lira *et al.,* 2018). Los nanomateriales se definen como partículas a nanoescala cuyo tamaño oscila entre 1-100 nanómetros (Venkatesh *et al,* 2018). Las aplicaciones más comunes de la nanotecnología han sido en forma de nanopesticidas (Np) y nanofertilizantes (Nf) (Chhipa, 2017); los primeros consisten en la encapsulación de insecticidas, fungicidas y herbicidas; diversos autores han reportado que la encapsulación de los anteriores mostraron que la dosis necesaria y el riesgo ambiental se reducen significativamente además la eficiencia de éstos aumenta (Caballero *et al.,* 2019; Memarizadeh *et al.,* 2014; Mattos *et al.,* 2016; bin Hussein *et al.,* 2005). Por otro lado los Nf son nanomateriales que pueden proporcionar uno o más nutrientes para ayudar al crecimiento y desarrollo de las plantas (Liu y Lal, 2015; Chhipa, 2017). Diversos autores han estudiado los efectos de los Nf en la agricultura, por ejemplo, se emplearon NPs de hidroxiapatita modificadas superficialmente con urea como fuente de N, éstas mostraron la capacidad de liberación lenta y controlada durante un tiempo prolongado (Kottegoda *et al.,* 2011), en otro estudio se desarrollaron y aplicaron NPs de Ca y P en semillas de *Glycine max* y los resultados obtenidos mostraron un efecto positivo con un aumento de 33% en el rendimiento de la semilla (Liu y Lal, 2014). La aplicación de NPs de óxido de hierro en el cultivo de soya redujo la clorosis ocasionada por la deficiencia de hierro y aumentó la clorofila en las hojas (Ghafariyan *et al.*, 2013). Por otra parte, se aplicaron NPs de CeO_2 al cultivo de pepino a una concentración de 400 mg Kg^{-1}, estas NPs incrementaron el contenido de globulina, sin embargo al combinar NPs CeO_2 + NPs ZnO el contenido de almidón aumentó significativamente comparado con el control (Zhao *et al.,* 2014). La aplicación de NPs Ag intervino en el crecimiento y metabolismo de *Bacopa monnieri* aumentando los niveles de proteína y carbohidratos esto ocasionado porque NPs indujeron estrés a las plantas tratadas (Krishnaraj *et al.*, 2012). En semillas de tomate expuestas a NPs SiO_2 se mejoró el porcentaje y tiempo de germinación, vigor, peso seco y fresco de las plántulas de tomate (Siddiqui y Al-Whaibi, 2014). En este contexto, los resultados obtenidos con el uso de NPs son satisfactorios, sin embargo, durante la síntesis de las NPs, debido a su alta energía y tamaño superficial, éstas tienden a aglomerarse dificultando la dispersión (Betancourt *et al.,* 2010) y por ello algunas investigaciones se han enfocado en la búsqueda de métodos de modificación o encapsulamiento de NPs con compuestos orgánicos e inorgánicos (Hong *et al.*, 2006; Siddiquey *et al.*, 2008; Grasset *et al.,* 2003). Las investigaciones anteriormente realizadas nos llevaron a determinar el efecto de la NPs en el crecimiento y desarrollo de las plantas de tomate tomando en cuenta los factores de morfología de las NPs, modificación superficial con maltodextrina (MDX y la forma de aplicación. Considerando todo lo anterior se planteó el siguiente objetivo:

Objetivo general:

Determinar el efecto de NP de ZnO, así como estudiar el efecto de la modificación superficial de las NPs con un polisacárido obtenido de la hidrólisis del almidón de maíz (maltodextrina) en el cultivo de tomate bajo condiciones de agricultura protegida.

Hipótesis:

La aplicación de nanopartículas de ZnO y TiO2 estimularán el crecimiento y desarrollo del cultivo de *Solanum lycopersicum*.

REVISIÓN DE LITERATURA

La Nanotecnología

La nanotecnología es una disciplina, relativamente, reciente que desarrolla materiales en escala nanométrica (1-100 nanómetros), y debido a su tamaño, los científicos e ingenieros alrededor del mundo descubren fascinantes propiedades y aplicaciones que proveen de nuevas herramientas para el diseño de materiales en campos como la electrónica, física, química, biología molecular, medicina, medio ambiente, textil, farmacéutica, industria alimenticia y agricultura. La nanotecnología es definida como el diseño, caracterización y aplicación de estructuras, dispositivos y sistemas mediante el control de la forma, el tamaño y las propiedades de la materia a escala nanométrica (Mendoza y Rodríguez, 2007: Venkatesh *et al.*, 2018).

En el campo del medio ambiente, por ejemplo, los nanomateriales se han empleado para el tratamiento de aguas residuales y descontaminación de suelo así como el uso de nanosensores que son capaces de detectar sustancias dañinas (Theron *et al.*, 2008). En el sector energético se ha buscado mejorar el almacenamiento de esta misma mediante el desarrollo de aislantes térmicos más eficientes, en medicina los avances tecnológicos con el uso de nanomateriales han sido muy importantes para el tratamiento de enfermedades como el cáncer, ya que mediante el uso de nanopartículas se transportan fármacos que pueden ser dirigidos a sitios específicos del cuerpo humano, también se han desarrollado biosensores que detectan sustancias como la glucosa o destruyen células tumorales así mismo se han usado nanopartículas con propiedades antimicrobianas y antisépticas (Sels y Van, 2017; Wang *et al.*, 2013; Betancourt *et al.*, 2014). En ingeniería de sistemas computacionales la nanotecnología ha permitido el desarrollo de nanocables y conductores que permiten una mayor rapidez, materiales con más flexibilidad, mayor almacenamiento y reducción de tamaño de computadoras (Kaewkamnerdpong, 2005).

Aplicaciones de la Nanotecnología en la Agricultura

A lo largo del tiempo, el sector agrícola siempre ha sido foco de atención para la aplicación de nuevas tecnologías, esto debido al aumento acelerado de la población mundial, lo que representa un aumento en la producción de alimentos para satisfacer las necesidades de los consumidores, además del aumento acelerado de población se suman otros como son el cambio climático, sequías, aumento del uso de energía y sobre todo la perdida de la fertilidad de los suelos como consecuencia del uso indiscriminado de fertilizantes químicos que no solo dañan el medio ambiente sino la salud humana (Cheng *et al.*, 2016). Esto ha incentivado la búsqueda de tecnologías para el desarrollo de plantas que tengan mayor rendimiento y resistencia a factores bióticos y abióticos, que además sean ecoamigables ya que, en la actualidad los consumidores han prestado mayor atención a la inocuidad alimentaria. La biotecnología aplicada a la agricultura ha permitido el desarrollo de semillas mejoradas, transferencia de genes y/o micropropagación *in vitro*, sin embargo, en la última década la nanotecnología ha surgido como una esperanza para lograr una agricultura sostenible convirtiendo las prácticas agrícolas convencionales en agricultura de precisión (Chhipa, 2017). Para lograr un incremento en el rendimiento de los cultivos de interés agrícola, se emplean fertilizantes y pesticidas convencionales químicos en cantidades altas y durante todo el ciclo del cultivo los cuales presentan una baja eficiencia lo cual ocasiona contaminación de aguas subterráneas, disminución de la flora microbiana de los suelos causando infertilidad de suelos además de causar resistencia de plagas y enfermedades (Srilatha, 2011). Por lo tanto los científicos han buscado alternativas para desarrollar fertilizantes que ayuden a mejorar la productividad de las plantas sin dañar la calidad ni alterar la salud del consumidor final y/o contribuir a la contaminación ambiental. Las aplicaciones de la nanotecnología en la agricultura son, precisamente, nanosensores, nanopesticidas y nanofertilizantes (Figura 1).

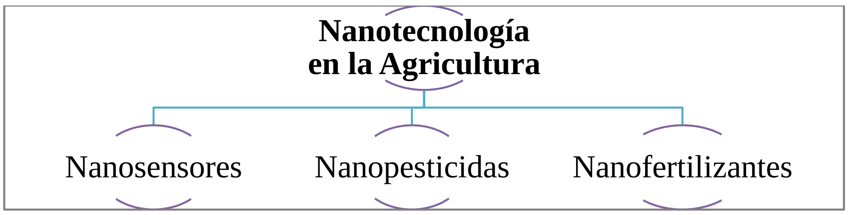

Figura 1. Aplicaciones de la nanotecnología en la agricultura: para el manejo de nutrición y detección/manejo de plagas y enfermedades.

Nanosensores

Los nanosensores, también conocidos como nanobiosensores, tienen un rango de 1-100 nm que integra un elemento biológico (enzima, ADN) que puede reconocer el analito (sustrato de enzima, ADN complementario), por ello es una herramienta innovadora con capacidad de proporcionar información en tiempo real sobre las condiciones del suelo y de la planta, así como indicar la ubicación exacta del patógeno o pesticida (Chhipa y Joshi, 2016). Los nanosensores que se han desarrollado hasta ahora, se pueden ver en la Figura 2. Dichos dispositivos se emplean para el monitoreo de las condiciones del suelo como humedad y pH, pueden ser programados para liberar hormonas de crecimiento a la plantas además son capaces de alertar sobre cambios de las condiciones ambientales (Omanović-Mikličanina y Maksimović, 2016). El desarrollo de nanosensores de NPs de sílice (NEMS) mostró eficiencia para la detección de *Xanthomonas axonopdis* reponsable de la mancha bacteriana en solanáceas (Yao *et al.*, 2009) asimismo fue capaz de minimizar los efectos del mildiu polvoriento en cucurbitáceas (Park *et al.*, 2006). También se ha reportado que nanosensores con NPs-Cu ayudan a controlar patógenos como *Fusarium sp*., *Phytopthora*, *Xanthomonas oryzae* y *Xanthomonas campestris* (Giannousi *et al.*, 2013).

Los nanosensores también son usados para la detección de compuestos volátiles (nariz electrónica) mediante los cuales fue posible discriminar plantas sanas y afectadas por hongos (Laothawornkitkul *et al.*, 2010; Ghaffari *et al.*, 2010). Los nanotubos de carbono también se han empleado para nanosensores para la detección de residuos de plaguicidas (Sharon y Sharon, 2008).

En la industria alimenticia (biosensor de matriz) se usan enzimas obtenidas de plantas para evaluar la actividad antioxidante así como la contaminación por fenoles en alimentos procesados y empaques (Medina-Pérez *et al.*, 2019).

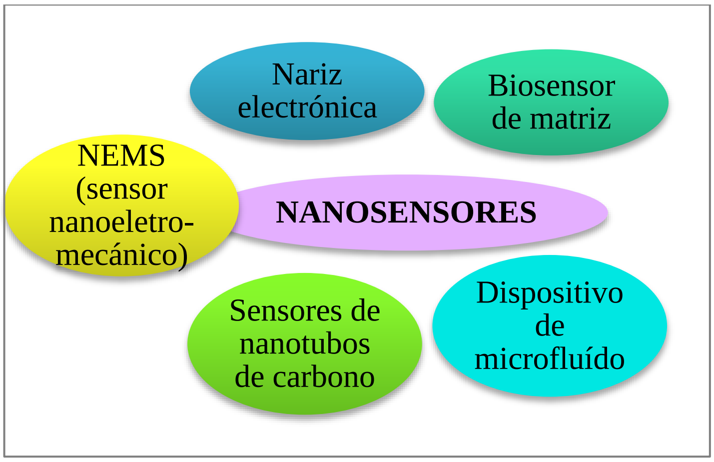

Figura 2. Tipos de nanosensores usados en agricultura e industria alimentaria (Sozer y Kokini, 2009).

Nanopesticidas

Medina-Pérez *et al*. (2019) menciona que los nanopesticidas son un método para lograr una agricultura de precisión por lo que se han desarrollado nanoencapsulaciones para equilibrar y optimizar las dosis aplicadas de plaguicidas convencionales. Los nanopesticidas se definen como partículas pequeñas que contienen ingredientes activos (i.a) de pesticidas o bien compuestos con propiedades pesticidas, asimismo, estos nanomateriales tienen ventajas que los hacen únicos, como la liberación lenta durante periodo prolongado, incrementan la dispersión y estabilidad de los i.a, reduce la pérdida por escurrimiento, proporciona los i.a de manera dirigida (Bergeson, 2010; Chhipa, 2017; Khot *et al.*, 2012). En la tabla 1se recopila información sobre los efectos de la aplicación de pesticidas y compuestos con dichas propiedades en forma de nanopesticidas.

Tabla 1. Uso de pesticidas nanoencapsulados y su impacto para el control de patógenos.

Pesticida y/o compuesto	Efecto	Referencia
Quitosan/Paraquat	Disminuyó la toxicidad y mejoró la dinámica del herbicida.	Grillo *et al.*,, 2015
Aceite de neem	Control de la incidencia del ácaro *Sarcoptes scabiei* var. Cuniculi en condiciones in vitro.	Xu *et al.*, 2010
Permetrina	Mortalidad del 100% de larvas de mosquitos C*ulex quinquefasciatus*.	Anjali *et al.*, 2010
Polietilenglicol (PEG)/aceite de ajo	Eficacia del 80% sobre el control del gorgojo de la harina *(Tribolium castaneum*).	Yang *et al.*, 2009
Benzoilfenilurea	Tasa de mortalidad elevada del gusano del algodón (*Spodoptera littoralis*).	Elek *et al.*, 2010
Triclosán	Mayor actividad biocida comparado con soluciones acuosas de triclosán.	Zhang *et al.*, 2008
Ethiprole	Penetración mejorada a través de la planta mayor control de áfidos.	Boehm *et al.*, 2003
Validamicina/carbonato de calcio	Mejor eficacia fúngica contra *Rhizoctonia solani.*	Qian *et al.*, 2011
Quitosan	Reducción de germinación de esporas fúngicas.	Chookhongkha *et al.*, 2013;
Ag	Reducción *Xanthomonas campestris, Xanthomonas perforans,*	Rajesh *et al.*, 2012
Cu	Inhibición de crecimiento bacteriano y actividad antifúngica	Bramhanwade *et al.*, 2016; Giannousi *et al.*, 2013

Nanofertilizantes

Los Nf son definidos como nanomateriales con medidas de 1-100 nm, que son capaces de suministrar uno o más nutrientes a las plantas con la finalidad de ayudar a su crecimiento y desarrollo (Chhipa, 2017; Liu y Lal, 2015). El interés particular del desarrollo y aplicación de Nf se enfoca en la reducción del uso de fertilizantes químicos y ayudar a mejorar el desarrollo de los cultivos (Singh *et al.*, 2017) además ofrecen ventajas como la mejora de la eficiencia de fertilizantes convencionales, reduce la pérdida de nutrientes y por ende minimiza el impacto ambiental de los fertilizantes químicos, los Nf son capaces de mejorar el rendimiento y calidad de los cultivos (Liu y Lal, 2015). Actualmente se desarrollan NPs que usan como portadores de elementos o sus óxidos, los Nf se dividen en tres categorías: macronanofertilizantes, micronanofertilizantes y fertilizantes nanoparticulados (Medina-Pérez *et al.*, 2019; Liu y Lal, 2015; Chhipa, 2017).

Macronanofertilizantes

En esta categoría se encuentran los elementos que la planta necesita en cantidades relativamente altas como son el N, P, K, Ca, Mg, S. Muchos investigadores han desarrollado y estudiado los Nf de macronutrientes usándolos en laboratorio y campo. Liu y Lal (2015) han revisado el uso de Nf en la agricultura de manera integral. La zeolita recubierta con urea, fue usada como fuente de N y mostró capacidades de liberación lenta y controlada de N (Kottegoda *et al.*, 2011). Liu y Lal (2014) estudiaron nanopartículas de Ca y P las cuales mostraron un incremento de 20 y 33% en el rendimiento de semilla de *Glycine max* en comparación con los fertilizantes convencionales. Liu et al. (2005) desarrollaron NPs de calcio en el cultivo de *Arachis hypogaea* y estos mejoraron 15% la biomasa. En la tabla 2 se muestran los diferentes tipos de micronutrientes utilizados en la agricultura.

Tabla 2. Diferentes macronutrientes empleados para el desarrollo de Nf y su impacto en cultivos agrícolas.

Macronutriente	Cultivo	Impacto
N (HA-urea) (CLT-NH_4)	Raigrás y Maíz	Liberación lenta y controlada durante 30 días en raigás (Kottegoda *et al.,* 2011). Aumento de rendimiento (14%) en maíz (Malekian *et al.*, 2011)
P (HA -Ca)	Soya	Crecimiento y rendimiento mayor comparado con el control de Ca $(H_2PO_4)_2$. (Liu y Lal, 2014
K Zeolita-K	Crisantemo	Aumento del rendimiento y disminución de lixiviación de K, control usado KCl (Hershey *et al.*, 1980)
Ca Ca_3P2O_8	Maní	Crecimiento, rendimiento y calidad aumentaron significativamente respecto al testigo $Ca(NO_3)_2$. (Tarafdar *et al.*, 2012)
Mg NPs-Mg	Guisante de ojos negros	Aumento del peso de la semilla, mayor concentración de Mg en hojas y tallos, resultados mejores al testigo de $MgSO_4$. (Delfani *et al.*, 2014)

HA=hidroxiapatita, CLT=clinoptilolita

Micronanofertilizantes

Los micronutrientes a diferencia de los macros, son requeridos en concentraciones mucho más bajas (≤100ppm), sin embargo esto no significa que dejen de ser esenciales (Marschner, 2011). Delfani et al. (2014) utilizaron NPs de Fe y Mg en guisantes de ojos negros y obtuvieron un aumento del 10% en el contenido de clorofila en las hojas; en *Glycine max*, el contenido de clorofila se incrementó con una concentración de 30-60 ppm (Ghafariyan *et al.,* 2013). Nanopartículas de Mn en el cultivo de *Vigna radiata* aumentaron en 52% la longitud de la raíz, 38% de longitud de brote y 38% la biomasa (Pradhan *et al.,* 2013). Las NPs-Cu han aumentado un 35% la fotosíntesis en algas *Egeria densa* (Nekrasova *et al.,* 2011) y aumentó un 40% el crecimiento de lechuga (Shah y Belozerova, 2009). Las NPs de Molibdeno aumentaron la actividad microbiana y crecimiento de semilla en garbanzo (Taran *et al.,* 2014). En cuanto al Zn, es un micronutriente esencial encargado de regular las actividades enzimáticas en las plantas, en estudios con aplicación de ZnO mostraron mejora significativa en la biomasa, longitud de raíz, contenido de clorofila, proteínas, y actividad de ciertas enzimas como fitasa, fosfatasa ácida y alcalina (Lin y Xing 2007; Mahajan *et al.,* 2011; Tarafdar *et al.,* 2014). En la tabla 3 se muestran los diferentes tipos de macronutrientes nanoparticulados utilizados en la agricultura.

Tabla 3. Diferentes micronutrientes empleados para el desarrollo de Nf y su impacto en cultivos agrícolas.

Micronutriente	Cultivo	Impacto
Fe NPs-Fe_3O_4	Soya	Aumento de clorofila(Ghafariyan *et al.,* 2013)
Mn NPs-Mn	Frijol mungo	Aumento de longitud de brote, contenido de clorofila y tasa fotosintética (Pradhan *et al.*, 2013)
Mo NPs-Mo	Garbanzo	Mejoramiento de nódulos, bacterias simbióticas, y actividad antioxidante así (Taran *et al.*, 2014)
Ce NPs-CeO_2	Pepino	Incremento de almidón, globulina, flavonoides y fenoles (Zhao *et al.*, 2014)
Cu NPs-Cu	Lechuga	Aumento del crecimiento de raíz, brote, contenido de N (Shah y Belozerova, 2009)
	Maleza brasileña	Aumenta la tasa fotosintética (Nekrasova *et al.*, 2011)
Zn NPs-ZnO	Frijol mungo, pepino y maní	Mejora rendimiento y crecimiento de frijol (Mahajan *et al.*, 2011). Aumenta el almidón, glutelinas y biomasa seca en pepino (Zhao *et al.,* 2014). Aumento de clorofila, mejor germinación y vigor de semilla de maní (Prasad *et al.*, 2012)

Fertilizantes nanoparticulados

En esta categoría se encuentran elementos que no son esenciales para las plantas y son conocidos como elementos benéficos ya que su aplicación ha mostrado respuestas positivas en cultivos a los que se aplican, varios investigadores han informado sobre su efecto positivo sobre la eficacia de la fotosíntesis, aumento de clorofila y proteínas así como mejoras en la actividades enzimáticas (Yang *et al.*, 2007). En la tabla 4 se pueden observar los distintos nutrientes benéficos empleados para el desarrollo de nanopartículas.

Tabla 4. Diferentes nutrientes benéficos empleados para el desarrollo de fertilizantes nanoparticulados y su impacto en cultivos agrícolas.

Nutriente benéfico	Cultivo	Impacto
Ti NPs-TiO_2	Espinaca (*Spinacia oleracea*)	Aumentó la actividad de la rubisco, aumenta la trasferencia de electrones y la conversión de energía luminosa (complejo D1) (Gao *et al.*, 2008; Su *et al.*, 2009)
	Trigo (*Triticum aestivum*)	Mejoró la germinación y el alargamiento del sistema radicular, aumentó el contenido de gluten y almidón (Laure *et al.*, 2012; Jaberzadeh *et al.*, 2013)
Au NPs-Au	Mijo perla (*Pennisetum glaucum)*	Efectos positivos en el porcentaje de germinación y crecimiento de las plántulas así como aumento de la biomasa (Parveen *et al.*, 2016)
Si **NPs-SiO_2**	Tomate (*Lycopersicum esculentum*)	Disminución del tiempo de germinación, aumentó porcentaje de germinación, vigor de semilla, biomasa fresca y seca de plántula, el control fue con aplicación de sílice a granel (Siddiqui y Al-Whaibi, 2014)
NPs-SiO_2	Maíz (*Zea maíz*)	Aumentó el porcentaje de germinación (95.5%) mayor concentración de nutrientes en las semillas expuestas a Si y aumento del rendimiento, tratamiento control con aplicación de sílice a granel (Suriyaprabha *et al.*, 2012)
Ag **NPs-Ag**	*Arabidopsis thaliana*	Incremento de ROS y crecimiento de raíz, activó genes implicados en la proliferación celular y el metabolismo (Syu *et al.*, 2014)

ARTICULO

Effects of the Morphology, Surface Modification and Application Methods of ZnO-NPs on the Growth and Biomass of Tomato Plants

molecules

MDPI

Article

Effects of the Morphology, Surface Modification and Application Methods of ZnO-NPs on the Growth and Biomass of Tomato Plants

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Abstract: Benefits of nanotechnology in agriculture include reduced fertilizer loss, improved seed germination rate and increased crops quality and yield. The objective of this research was to evaluate the effects of zinc oxide nanoparticles (ZnO-NPs), at 1500 ppm, on tomato (*Solanum lycopersicum* L.) growth. ZnO-NPs were synthetized to produce either spherical or hexagonal morphologies. In this research, we also studied two application methods (foliar and drench) and nanoparticles' (NPs) surface modification with maltodextrin. The results obtained indicate that ZnO-NP-treated tomato plants significantly increased plant height, stem diameter and plant organs (leaves, stem and root) dry weight compared to plants without NP treatment.

Keywords: greenhouse crops; surface modification; maltodextrin; plant biomass

Introduction

Nanotechnology (NT) is a multidisciplinary science that has gained importance in agriculture and other economic activities including industries such as the textile, cosmetics, medicine, electronics, food production and hydraulics industries [1–7]. Nanotechnology in agriculture has attained acceptance in the last decade because it has arisen as a technological advancement to produce different tools; for example, nanoproducts can be used as nanosensors for stress detection caused by biotic and abiotic factors, nanopesticides to increase pesticide efficiency [8] and nanofertilizers (Nf). Nanofertilizers have been defined as modified fertilizers that may improve crop productivity and quality, as well as soil fertility [9]. It is known that agriculture faces different challenges that threaten food production sustainability: climatic change, population increase and the extensive use of chemicals that pollute soil, water and plants, causing ecological imbalance and directly affecting animals and humans [10]. The particular interest in Nf is to reduce the rate of chemical fertilizers required to achieve increased crop growth and yield [11]. Zinc (Zn) plays a key role in enzymatic activation for protein synthesis in plants. It is considered an essential microelement because it is required in small quantities but it is also crucial for vegetative development [12]. This nutrient acts as a precursor in phytohormones like auxins, which influence cell elongation and division, furthermore, Zn is essential for photosynthesis and facilitates carbohydrate metabolism in plants because Zn stabilizes or activates the proteins involved in these processes [13].

Zinc, along with iron, copper, silver and titanium, is among the metals most commonly used for the synthesis of nanoparticles (NPs). Numerous studies have reported that plant development and growth respond to ZnO-NP application and that they have the capacity to inhibit and control some diseases [11].

Tarafdar mentioned that ZnO-NPs increase the activity of phytase and alkaline and acid phosphatases, contributing to phosphorus solubilization and plant uptake [14]. The ZnO-NPs are also reported to (1) increase by 21.6% the number of shoots in chickpea seedlings [15], (2) increase by 10% the germination of cucumber seeds compared to the control (Zn) [16], (3) stimulate flowering up to 14 days earlier in onions [17], and (4) increase the length of the main and lateral roots by 17% and 26%, respectively, in tobacco plants treated with ZnO-NPs compared to plants treated with $ZnSO_4$ [18]. The application of ZnO-NPs to *Setaria italica* increased seed oil and nitrogen content and plants exhibited higher water stress tolerance [19]. There are many benefits from the use of ZnO-NPs; nevertheless, it should be noted that they present a photo-catalytic activity that gives rise to oxidative reactions in the particle's surface, unleashing free radicals that promote degradation ([20].

However, ZnO-NPs exhibit stability and dispersion problems due to their nanometric size. NPs often gather together causing particle agglomeration [21] due to their wide surface area, therefore presenting poor dispersion [22]. In order to decrease NPs' agglomeration and oxidation, and to improve their dispersion and stability, scientists have investigated different methods of NP coating or surface modification. Several works on ZnO-NPs' modification or coating with aggregated organic and inorganic compounds and polymeric matrixes have been reported [23–26]. ZnO-NP modification with different types of modifiers is summarized in Figure 1.

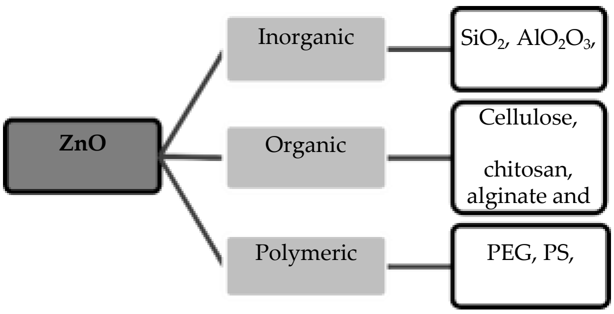

Figure 1. Used agents for surface modification of ZnO. PEG = polyethylene glycol; PS = polystyrene; PMMA = polymethylmethacrylate.

Maltodextrin (MDX) is a polysaccharide derived from starch hydrolysis and its main application is in the food industry as an artificial sweetener [27]. It is also used in agriculture as a constituent in some insecticides and acaricides [28]. It has been shown that NPs' morphology affects their optical, electrochemical, sensory, thermal and mechanical properties. This morphology effect is a phenomenon known as magnetic anisotropy [29]. Particle morphology also contributes to the dispersion, degradation process, stability and compatibility of ZnO-NPs [30]. However, despite the previous investigations conducted in this field, the ZnO-NPs' morphology effect, as well as the effect of surface modification, have not been thoroughly explored.

Mexico is one of the world's main tomato (*Solanum lycopersicum* L.) producers and exporter [31]. Tomato nutritional value is high and is appreciated due to its vitamins, minerals, sugars, proteins, fiber, organic acids and lycopene, an antioxidant with anticarcinogenic qualities [32]. The objective of this research was to determine the effect of ZnO-NPs with two different morphologies (spherical or hexagonal) in interaction with MDX modification and two application methods (foliar or drench), on the growth parameters of tomato plants.

Materials and Methods

1.1. NPs Synthesis

Two ZnO-NPs morphologies (spherical and hexagonal) were prepared using 26.33 g of Zn $(O_2CCH_3)_2$, 1700 mL of ethanol and 300 mL of deionized water. Immediately, 5.36 mL of triethanolamine (TEA) and 1.42 mL of n-propylamine (NPA) were added. The reaction was conducted at 65 °C in reflux and with constant stirring for 6 h (for hexagonal NPs synthesis) or 12 h (for spherical NPs synthesis). After the system was cooled, the material obtained was rinsed, centrifuged and dried under a vacuum for 12 h at 80 °C. The precipitation method described by Hsieh [33] was used in this research.

1.2. ZnO-NPs' Surface Modification

The ZnO-NPs' surface modification was conducted using an MDX:ZnO-NPs 1:1 molar ratio (1.5 g:1.5 g). Ethanol was used as a dispersion agent. The reaction was carried out at 65 °C in reflux and with constant stirring for 6 h. The system was immediately cooled. The modified ZnO-NPs were decanted and dried out for 12 h at 80 °C for their further analysis.

1.3. ZnO-NPs Characterization

The infrared analysis (FT-IR) was carried out using Nicolet iS50 equipment (Thermo Fisher Scientific Inc., Madison, WI, USA.) KBr tablets were prepared with ZnO-NPs samples to identify the ZnO-NPs and the respective modifying agent. The XRD analysis was conducted with a Siemens D-500 diffractometer (SIEMENS, Munich, GER) with CuKα radiation to identify the crystalline phase in both modified and non-modified ZnO-NPs. The morphology and surface modification of ZnO-NP samples were carried out through a high-resolution transmission electronic microscope (HRTEM) Titan 80–300 kV (FEI Company, Hillsboro, OR, USA).

1.4. Plant Material and Management

The effect of ZnO-NPs was measured at experiment termination on tomato cv Clermon plants grown under greenhouse conditions. Seeding was carried out on 13 February, 2018, using 1 L containers filled with sphagnum peat.

Two NP application methods were used: drench and foliar. Drench was conducted before planting with 50 mL of a 1500 ppm ZnO-NPs solution dispersed by a sonicator (SONICS model VC505) for 15 min at 38% Abs. Foliar application was conducted manually five weeks after planting, when leaves were fully developed. Plants were transplanted nine weeks after seeding in 10 L containers with a mixture of sphagnum peat and perlite (60%:40% *v*/*v*). A second ZnO-NP application was performed five weeks after transplanting, both via drench or foliar.

Plants were fed with a Steiner's [34] nutrient solution adjusted to the plant's phenological stage through a drip irrigation system with two 4 L/h emitters. Lateral shoots and older foliage were pruned weekly. The experiment was terminated on August 2018.

1.5. Growth and Plant Organs Biomass Measurement

Plant height and stem diameter were measured at experiment termination, while pruned leaves were collected and placed on a drying oven at 65 °C for 48 h prior recording the dry weight. Root and stem dry weight was measured at experiment termination and after dried in an oven, as previously described, for leaves.

1.6. Statistical Data Analyses

Treatments were arranged in a randomized block design using a factorial arrangement with 12 treatments and 5 replications, one plant per replication. The factors considered were: two ZnO-NPs morphologies (spherical and hexagonal, plus a control with no NPs application), two application methods (drench and foliar) and NPs surface modification with MDX (modified and non-modified). The software used for the statistical analysis was SAS (SAS Version 9.4, SAS Institute, Cary, NC, USA) and a means comparison test was conducted according to Tukey's multiple comparison test ($p < 0.05$).

Results and Discussion

1.7. ZnO-NPs Characterization

The HRTEM micrograph of the ZnO-NPs reveals the presence of spherical particles of <30 nm and with an even distribution size (Figure 2a). The larger particles are attributed to particle agglomeration. The particle size distribution histogram indicates that it ranges from 11 to 40 nm, with an average of 22.5 nm (Figure 2b). Additionally, hexagonal NPs (Figure 3a–b) with single particles ranging from 60 to 120 nm and an average of 85 nm were obtained. ZnO-NPs' morphology, size and distribution observed in our study are similar to those reported by Hsieh [33], who performed the NPs synthesis with the precipitation method.

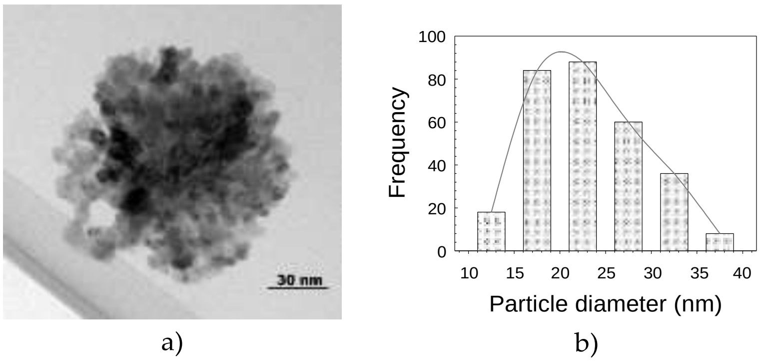

Figure 2. Transmission electron microscopy micrograph showing the spherical morphology of ZnO-NPs (**a**) and histogram of particle size distribution (**b**).

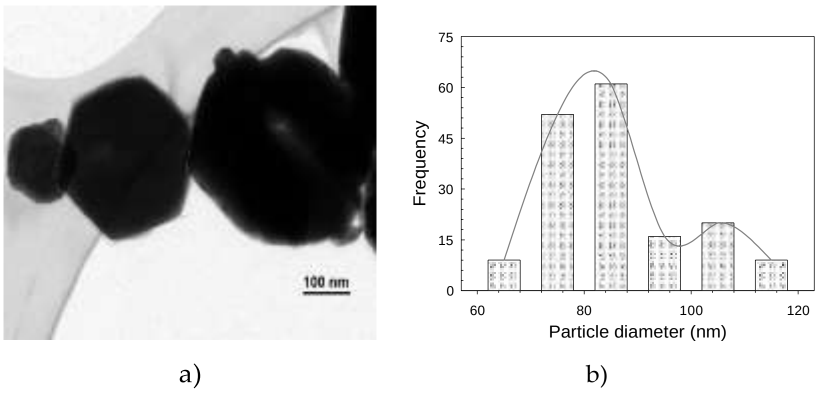

Figure 3. Transmission electron microscopy micrograph showing the hexagonal morphology of ZnO-NPs (**a**), and histogram of particle size distribution (**b**).

Figure 4a,b shows MDX-modified ZnO-NPs HRTEM images showing the presence of agglomerates as well as a fairly even MDX coating over the hexagonal and spherical NPs surface; Coating thickness was 0.92 and 1.22 nm for hexagonal and spherical NPs, respectively, suggesting that particle agglomeration does not affect surface modification.

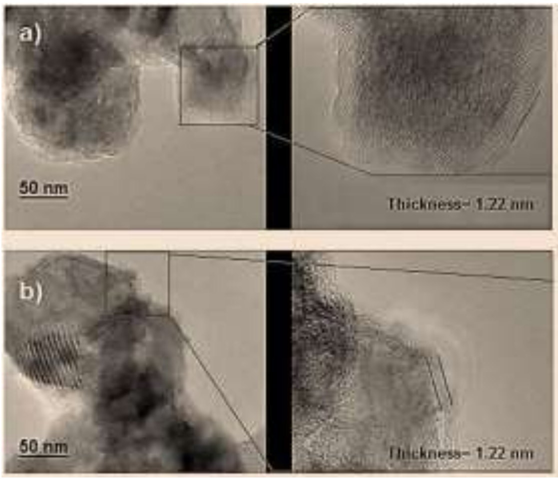

Figure 4. Transmission electron microscopy micrograph. Malotodextrine-modified ZnO-NPs with (**a**) spherical and (**b**) hexagonal morphology.

MDX-modified and non-modified NPs infrared spectra are shown in Figure 5. A belt appears at 450 cm^{-1} in both hexagonal and spherical nanoparticle spectrum due to the stretching of the ZnO bond. MDX-modified ZnO-NP spectra verifies that, in both morphologies, NPs were superficially coated with MDX. This was confirmed by MDX absorption bands at 1000 cm^{-1} as well as the band corresponding to ZnO which are present in both spectrums. In this way, FT-IR-aided, it is perceived that both ZnO-NPs synthesis and modification were properly carried out.

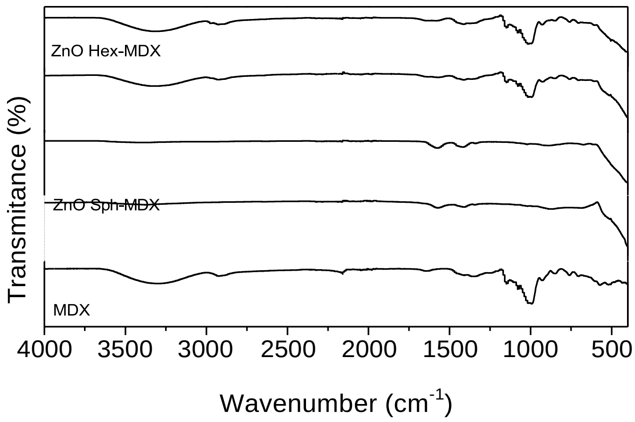

Figure 5. FT-IR spectrums of ZnO-NPs synthesized and modified by precipitation method.

In Figure 6, non-modified ZnO-NPs (Figure 6a,b) and MDX-modified ZnO-NPs (Figure 6c) corresponding X-ray (DRX) diffraction patterns are shown. Peaks present in DRX patterns match with wurtzite-type crystalline structures corresponding to the ZnO standard (JCPDS 36-1451) [35,36]. This means that the surface modification at which the NPs were subjected did not affect their crystalline structure [22,24].

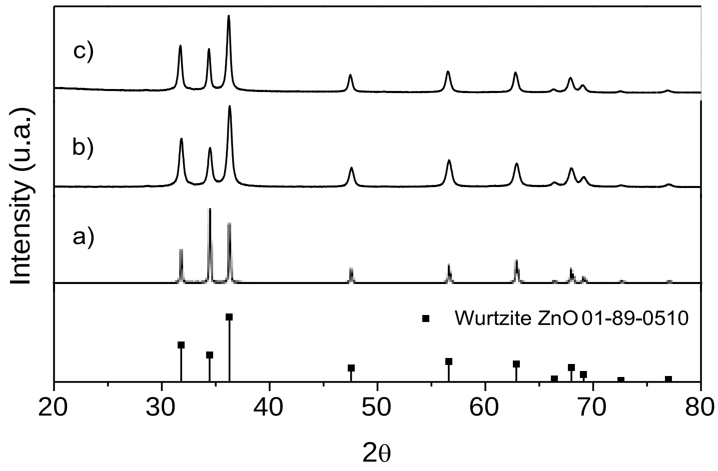

Figure 6. ZnO nanoparticle X-ray diffractogram. (**a**) Spherical ZnO-NP, (**b**) hexagonal ZnO-NP and (**c**) maltodextrin-modified ZnO-NP.

1.8. ZnO-NPs Effects on Plant Growth and Biomass

Nanoparticle morphology, surface modification with MDX and application method significantly affected tomato growth (Table 1). Stem diameter increased when hexagonal ZnO-NPs were applied, whilst surface modification with MDX and application method did not affect this parameter. However, an interaction between the assessed factors, such as the interaction between morphology and surface modification, and between morphology and application method, was observed (Table 1).

Table 1. Effect of different morphology, modification or non-modification with maltodextrine, and application methods of ZnO-NPs on different growth parameters of tomato plants.

	Stem Diameter (mm)	Plant Height (cm)	Leaf Dry Weight (g)	Root Dry Weight (g)	Stem Dry Weight (g)
Morphology					
Control	21.8 b	239 b	223.9 c	39.7 a	84.2 a
Spherical	21.9 b	230 b	253.2 b	36.7 b	85.4 a
Hexagonal	24.5 a	251 a	278.5 a	39.0 a	90.5 a
ANOVA	$p \leq <.0001$	$p \leq <.0001$	$p \leq <.0001$	$p \leq 0.0045$	$p \leq 0.1396$
MDX					
Non-Modified	22.4 a	234 b	245.3 b	36.2 b	82.8 b
Modified	23.1 a	246 a	258.4 a	40.9 a	90.5 a
ANOVA	$p \leq 0.0898$	$p \leq 0.0006$	$p \leq <.0001$	$p \leq <.0001$	$p \leq 0.006$
Application method					
Foliar	23.0 a	239 a	252.3 a	36.4 b	82.9 b
Drench	22.5 a	241.1 a	251.4 a	40.5 a	90.4 a
ANOVA	$p \leq 0.2243$	$p \leq 0.5336$	$p \leq 0.0035$	$p \leq <.0001$	$p \leq 0.0073$
Interactions					
M*MDX	$p \leq 0.0003$	$p \leq <.0001$	$p \leq <.0001$	$p \leq <.0001$	$p \leq <.0001$
M*A	$p \leq 0.0003$	$p \leq 0.015$	$p \leq 0.0006$	$p \leq <.0001$	$p \leq 0.0024$
MDX*A	$p \leq 0.5866$	$p \leq 0.3323$	$p \leq 0.7354$	$p \leq <.0001$	$p \leq 0.0301$
M*MD*A	$p \leq 0.2135$	$p \leq 0.00X05$	$p \leq 0.6123$	$p \leq <.0001$	$p \leq 0.6338$

M = morphology, MDX = maltodextrin, A = application. Different letters in same column are statistically different according to Tukey's multiple comparison test, ($p < 0.05$).

Plant height was higher when hexagonal, MDX-modified NPs where applied, however, the application method did not have a significant effect (Table 1). Every assessed factor interacted among them, having a significant influence on plant height (Table 1). Hexagonal ZnO-NPs, as well as MDX modification, significantly increased leaf dry weight; however, the application method, foliar or drench, did not affect this parameter. Root and stem dry weight displayed a similar response, since they were not affected by ZnO-NPs morphology; however, MDX surface modification as well as drench application increased root and stem dry weight (Table 1).

Stem diameter increased with spherical and hexagonal NPs application, but this occurred only without MDX. In comparison, there was no effect when modified NPs were applied (Figure 7a). Stem diameter increased when spherical and hexagonal NPs via foliar were applied. However, no effect was observed when a drench application was used (Figure 7b).

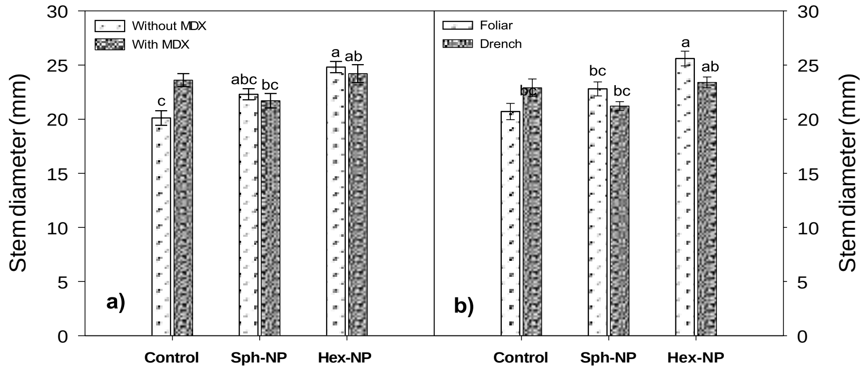

Figure 7. Effect of ZnO-NPs application on stem diameter. (**a**) Morphology*MDX interaction, (**b**) morphology and application method interaction. Bars represent the standard error of the mean. Different letters indicate significant differences according to Tukey's multiple comparison test ($p < 0.05$).

Plant height increased when MDX-modified hexagonal NPs were applied (Figure 8a) and when in control plants, when MDX but no NPs were applied via drench (Figure 8b), suggesting that the polysaccharide used in NP modification is acting as a plant growth stimulant. However, this effect may be enhanced when used along with ZnO-NPs. MDX has been used as an ingredient for very few agrochemicals like stimulants and has displayed beneficial effects in crop growth and development, as in lettuce, in which fresh biomass and yield increased 69% and 64%, respectively [37].

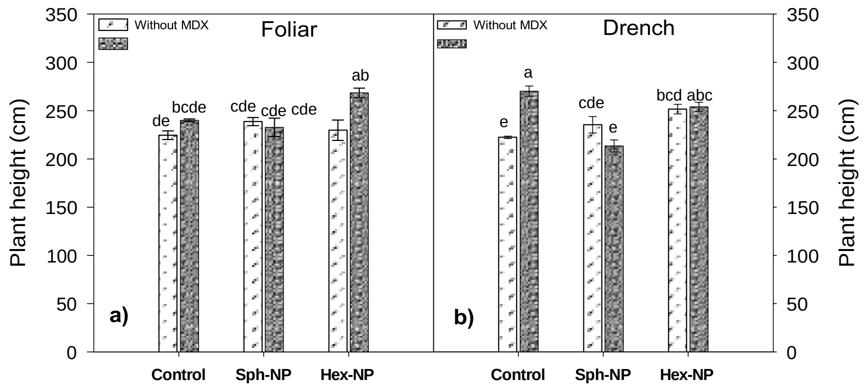

Figure 8. Effect of ZnO-NPs application on plant height. (**a**) Morphology*MDX*foliar application interaction, (**b**) Morphology*MDX*drench application interaction. Bars represent the standard error of the mean. Different letters indicate significant differences according to Tukey's multiple comparison test ($p < 0.05$). Sph = spherical, Hex = hexagonal.

Leaf dry weight increased with both hexagonal and spherical NPs application, although surface modification had no influence. However, MDX application without using NPs resulted in a substantial leaf dry weight increase compared to the control without MDX (Figure 9a), confirming that MDX has a growth regulation effect. Foliar dry weight increased with hexagonal and spherical NPs application, but it was more substantial when drench application with hexagonal NPs was used (Figure 9b).

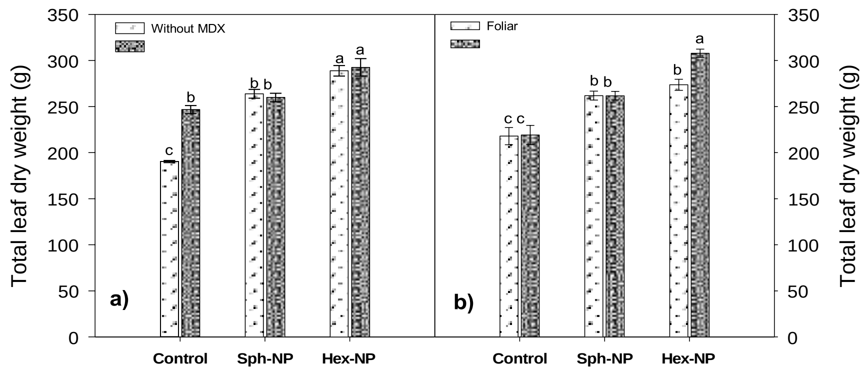

Figure 9. Effect of ZnO-NPs application on leaf dry weight. (**a**) Morphology and maltodextrin (MDX) modification interaction, (**b**) morphology and application method interaction. Bars represent the standard error of the mean. Different letters indicate significant differences according to Tukey's multiple comparison test ($p < 0.05$).

MDX without NPs application increased stem dry weight, nevertheless, using MDX and hexagonal NPs exhibited a slight further increase in stem dry weight (Figure 10a). On the other hand, a decrease in stem dry weight with NPs application, regardless of their morphology and application mode, was observed. There was an increase in stem dry weight in plants treated without ZnO-NPs, only with MDX, as long as it was by drench application (Figure 10b).

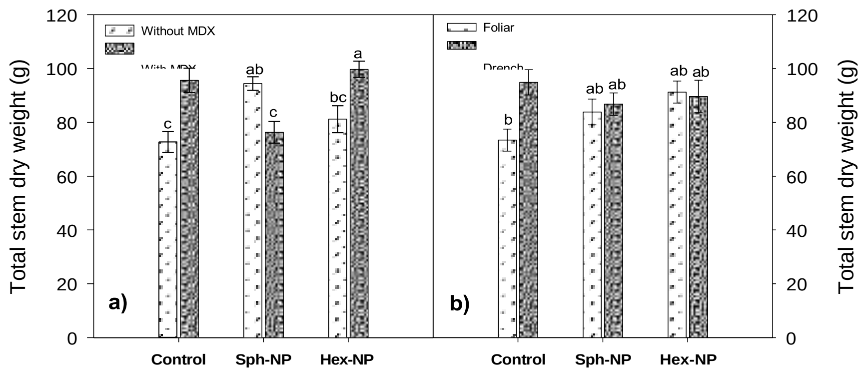

Figure 10. Effect of ZnO-NPs application on stem dry weight. (**a**) Morphology and maltodextrin (MDX) interaction, (**b**) morphology and application method interaction. Bars represent the standard error of the mean. Different letters indicate significant differences according to Tukey's multiple comparison test ($p < 0.05$).

MDX-modified hexagonal NPs increased root dry weight compared to control plants (Figure 11a). On the other hand, MDX application without ZnO-NPs drench-applied significantly increases root dry weight (Figure 11b). This result is similar to that on the stem dry weight. Syu reported that using spherical NPs in *Arabidopsis* plants and roots increased their growth compared to triangular NPs [38].

The positive effects of ZnO-NPs in plants, as observed in this research, have not been completely understood, however, greater absorption and retention of nutrients by plants has been reported when nanometric materials are applied [39], ZnO-NPs have the capacity of increasing enzyme activity, such as phytase, alkaline and acid phosphatase, which may contribute to nutrient solubilization like phosphorus [14]. Even though the effect of NP morphology is not very well understood yet, it is clear that is of utmost importance to take advantage of NPs' physical and chemical properties. Morphology, along with other characteristics that NPs should have, such as purity, crystalline state and size, determine the final product's yield, since NP distribution and ion release rate depend on them [40].

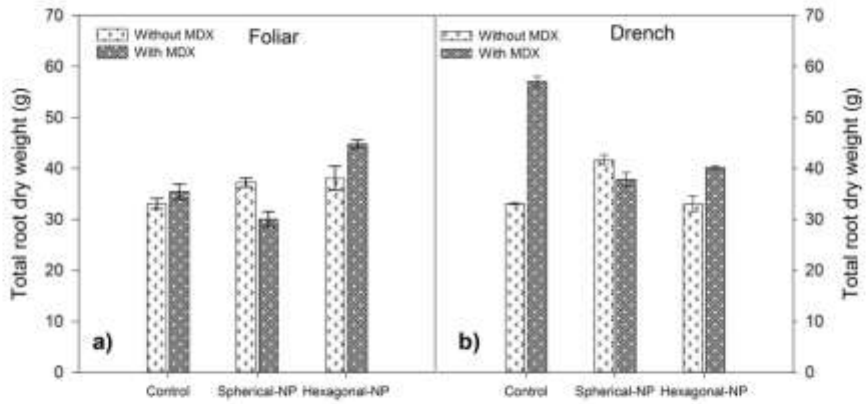

Figure 11. Effect of ZnO-NPs application on root dry weight. (**a**) Morphology*maltodextine (MDX)*foliar application interaction, (**b**) Morphology*MDX*drench application interaction. Bars represent standard error of the mean. Different letters indicate significant differences according to Tukey's multiple comparison test ($p < 0.05$). Sph = spherical, Hex = hexagonal.

The application of materials at a nanoscale has still unknown interactions with plants, however, it is more clear that the application of ZnO-NPs improves not only growth but also biomass accumulation, as reported in tobacco plants as ZnO positively affected the stem diameter, length and dry root weight [18]. Faizan reported enhanced growth, photosynthetic attributes, increased antioxidant activity and increased protein accumulation in tomato plants exposed to ZnO-NPs on untreated plants [41].

There are no studies in agriculture that prove either NPs' morphology or MDX coating effects. However, studies in medicine that explain that, as there is no control of the morphology in the synthesis of nanoparticulated systems, pharmaceuticals use surface coating to release the medical drugs in a controlled fashion, to avoid intoxicating consumers [42]. We hypothesize that the effect of surface-modified and MDX-coated ZnO-NPs on tomato plants may be due to this controlled released attribute.

4. Conclusion

ZnO-NP was synthesized with spherical and hexagonal morphologies and the procedure for modifying or coating NPs with maltodextrin was established. Tomato plants treated with ZnO-NP significantly improved plant height, stem diameter and dry weights, usually with hexagonal morphology and superficially modified. The modification of ZnO-NPs with MDX enhances the effect of ZnO-NPs, however, the application via drench of MDX without ZnO-NPs, in general, improved plant growth, supporting the hypothesis that MDX acts as a plant stimulant.

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ARTICULO

Morphology, Surface Modification and Application Form of NPs-ZnO Affect Growth, Yield, Gas Exchange Parameters and Nutrient Status in Greenhouse Tomato

MORPHOLOGY, SURFACE MODIFICATION AND APPLICATION FORM OF NPs-ZnO AFFECT GROWTH, YIELD, GAS EXCHANGE PARAMETERS AND NUTRIENT STATUS IN GREENHOUSE TOMATO

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Abstract
Nanotechnology is contributing to transform the conventional agriculture. Nanoparticles (NPs) of ZnO are reported to enhance plant growth, however, during the syntheses, NPs tend to agglomerate, affecting their dispersion. Agglomeration can be counteracted if NPs surface is modified, resulting in improved dispersion and stability. The morphology of NPs also affects their stability, and physical and chemical properties. In the present study, the surface of spherical or hexagonal NPs-ZnO was modified with maltodextrine (MDX) and either foliar or drench applied at 1500 ppm in soilless cultivated tomato. Hexagonal and spherical NPs increased plant growth, yield, fruit quality, fruit nutrient status and gas exchange parameters. Fruit P, K, Ca, Mg, Mn and Si concentration was higher in plants treated with hexagonal NPs-ZnO modified with MDX and applied by drench; however, Zn was higher when spherical or hexagonal no surface modified NPs were applied by either foliar sprays or drench. Significant but marginal increases in plant growth and yield were obtained by drench applications compared to foliar sprays. In general, spherical or hexagonal NPs produced similar results. Despite the yield increase, the morphology of the NPs, alone or combined with foliar or drench applications did not affect fruit yield or quality. MDX applied alone increased fruit yield and quality, although when combined with NPs morphology did not result in growth and yield improvement.

Keywords: Fruit quality, foliar applications, drench, fruit yield, macronutrient status, micronutrient status

1 Introduction

Soil fertility has been detrimentally affected due to the inappropriate use pesticides and mineral fertilizers. To reduce the impact of such practices on ecosystems and human health, scientists are in search of environmentally friendly alternatives as to the use of organic fertilizers and more biotic and abiotic resistant varieties as well as the use of biotechnological applications. Even though mineral fertilizers do increase crops´ yield, their increasing costs make them unsuitable for use under some conditions (Zamir, 2001); however, crop quality and soil fertility are detrimentally affected since mineral fertilizers may be leached at a rate ranging from 50% to 70% (Conley et al., 2009). Therefore, there is a need to modernize food production in order to decrease environmental impairment, which may be achieved by using cutting-edge technologies such as nanotechnology (NT). NT is a developing strategy and a promising alternative (Chhipa and Joshi, 2016) to reduce the use of agrochemicals while promoting plant growth, yield, and quality (Servin et al. 2015). NT has been applied in pest control (nanopesticides) and plant nutrition (nanofertilizers), thus, contributing to transforming the conventional agricultural practices into precision agriculture (Chhipa, 2017).

NPs of Ag, Ti, Cu, Fe, Mo, Si, and Zn have been developed and applied in agriculture. Zinc is a micronutrient that is a constituent or activator of enzymes and has a role in protein and AIA synthesis, carbohydrate metabolism, and membrane integrity (Broadley et al. 2012). Zinc oxide NPs (NPs-ZnO) at 1 g L^{-1} increased seed germination and drought tolerance in soybean (*Glycine max* L.) (Sedghi et al. 2013), while at 20 ppm resulted in a 40.8% and 76% increase in root and shoot biomass in mung bean (*Vigna radiata* L.) and at 1 ppm the increase was of 37.1% and 26.6%, respectively, in chickpea (*Cicer arietinum* L.) (Mahajan et al. 2011). In cucumber (*Cucumis sativus* L.), NPs-ZnO at 400 and 800 ppm resulted in increased starch and glutelin concentration, respectively, and in increased fruit Mg content (Zhao et al. 2014), while at 1000 ppm resulted in increased seed germination, seedlings vigor, earlier flowering, leaf chlorophyll content, and yield increased by 34% in peanut (*Arachis hypogea* L.) compared to the control plants treated with $ZnSO_4$ (Prasad et al. 2012). However, in spite of the benefits, during the syntheses, NPs tend to agglomerate due to their large area and surface energy, directly affecting their dispersion and final outcome (Hong et al. 2006). In order to counteract the agglomeration of the NPs, they can be superficially modified in order to improve their dispersion and stability without affecting their crystal structure (Betancourt et al. 2010).

Surface modification of NPs can be carried out by inorganic (Hong et al. 2006; Siddiquey et al. 2008) or organic compounds (Hong et al. 2006; Grasset et al. 2003) and polymer matrices (Xiong, 2010; Gu et al. 2012). Hong et al. (2006) modified the surface of NPs-ZnO with SiO_2 resulting in decreased photocatalytic activity, whereas when oleic acid was used as a surface modification agent there was improved compatibility between inorganic NPs and the organic matrix. Zhao et al. (2013a) used alginate as a modifying agent of NPs-ZnO, resulting in increased release of Zn into the soil solution and promoting Zn bioaccumulation in tissues of corn (*Zea mays* L.).

The morphology of NPs is another factor that intervenes in their stability, physical, chemical, and optical properties, microstructure, and purity, as along with NPs size, the morphology directly intervenes in their efficacy and the final outcome. In biomedical applications, for example, it is demonstrated that the biological functionality of a protein encapsulated in an NP depends on its morphology (Gagner et al. 2011); in Arabidopsis (*Arabidopsis thaliana* L.), three morphologies (spherical, triangular, and decahedral) of Ag-NPs were assessed by Syu et al. (2014), demonstrating that spherical and triangular NPs increased antimicrobial activity and decahedral NPs promoted root growth promotion.

Although the morphology and surface modification of NPs are important factors, they have not been studied considerably. In the present investigation, we modified NPs-ZnO with maltodextrine (MDX), a polysaccharide produced by the hydrolysis of starch obtained from corn, rice (*Oryza sativa* L.), potato (*Solanum tuberosum*), or wheat (*Triticum aestivum* L.). MDX has been used as a component of some plant biostimulants (Nori et al. 2019) and reports show that induces increases in fresh biomass, leaf area, and yield in lettuce (*Lactuca sativa* L.) (Hernández et al. 2015). The objective of the present study was to assess the effects of the morphology (hexagonal and spherical), the surface modification (with or without MDX) as well as the way of application of the NPs (drench and foliar) of NPs-ZnO on gas exchange parameters, fruit nutrient status, and plant growth and yield of soilless cultivated tomato (*Solanum lycopersicon* L.).

2 Materials and Methods

2.1 Synthesis and Characterization of MDX-Surface Modified Spherical or Hexagonal NPs-ZnO

The synthesis of the NPs-ZnO was carried out by the precipitation method (Cheng-Hsien, 2007), dissolving 26.33 g of Zn acetate in a mixture of deionized water (0.3 L), ethanol (1.7 L), TEA (5.36 mL) and n-propylamine (1.42 mL). The reaction was conducted at 65 ºC in reflux and with constant stirring for 6 hours for hexagonal NPs or 12 hours for spherical NPs. After cooling, NPs were rinsed, centrifuged, and dried under vacuum for 12 hours at 80ºC.

Surface modification was conducted by using a 1:1 molar mixture of MDX and NPs-ZnO with ethanol as the dispersing agent at 65ºC in reflux and constant stirring during 6 hours; after cooling, the modified NPs-ZnO were decanted by centrifugation and dried for 12 hours at 80ºC. High resolution transmission electron microscopy (FEI, model TITAN 80-300) showed that ZnO spherical NPs ranging from 11 to 40 nm and 22.5 nm on average, and hexagonal NPs ranging from 60 to 120 nm and 85 nm on average were obtained (for more details about NPs-ZnO synthesis and modification refer to Pérez-Velasco et al. (2020). X-ray Diffraction was performed using a Siemens D-500 diffractometer, in which the crystalline structure and the stability of both, modified and non-modified with MDX NPs-ZnO were observed, as well as for spherical and hexagonal NPs. Infrared spectroscopy_(FT-IR spectrometer, Thermo Scientific-Nicolet iS50) was performed to identify the bands corresponding to the NPs-ZnO and MDX. HRTEM images of MDX-modified NPs-ZnO exhibited a fairly even MDX coating over the hexagonal (0.92 nm thick) and spherical (1.22 nm) NPs surface. MDX-modified and non-modified NPs infrared spectrum showed a belt, due to stretching of the ZnO bond, appearing at 450 cm^{-1} in both hexagonal and spherical NPs spectrum. NPs-ZnO spectra verified that in both morphologies, they were superficially coated with MDX, which was confirmed by MDX absorption bands at 1000 cm^{-1} as well as the band corresponding to ZnO, suggesting that both NPs-ZnO synthesis and modification were properly conducted. X-ray diffraction patterns of non-MDX modified and MDX-modified NPs-ZnO showed peaks present that match with a wurtzite-type crystalline structure corresponding to ZnO standard, suggesting that surface modification did not affect their crystalline structure. For more details about ZnO nanoparticle X-ray diffractogram and FT-IR spectrums of NPs-ZnO, refer to Pérez-Velasco et al. (2020).

2.2 Plan Material and Growing Conditions

The study was conducted in a greenhouse at Universidad Autónoma Agraria Antonio Narro, in Northeast Mexico (25°23′42″ N Lat., 100°59′57″ W Long., 1743 m above sea level). Mean maximum, mean minimum, and mean temperature for the study duration were 23.2 °C, 12.4 °C, and 18.1 °C, respectively, while maximum, minimum, and mean relative humidity were 95%, 47%, and 72%, respectively. Mean seasonal photosynthetically active radiation was 370 µmol m^{-2} s^{-1}.

Tomato cv. Climstar seeds were sown on February 13, 2018 in 1 L containers filled with sphagnum peat; 9 weeks later, the plants were transplanted into 10 L containers filled with a mixture of sphagnum peat (60% v/v) and perlite (40% v/v). Initial medium pH and electrical conductivity (EC) were 5.7 and 0.8 dS m^{-1}, respectively.

Plants were irrigated with a complete nutrient solution (Steiner, 1961) containing, in meq L^{-1}, 12 NO_3^-, 1 $H_2PO_4^-$, 7 K, 9 Ca, 4 Mg, and 7 SO_4^{2-}. Micronutrients were provided, in mg·L^{-1}, at 5.3 Fe-EDTA, 0.4 Zn-EDTA, 2.6 Mn-EDTA, 0.5 Cu-EDTA, 0.2 B (Na_2 [B_4O_5 $(OH)_4$]·$8H_2O$), and 0.2 Mo (Na_2MoO_4). Nutrient solution pH was adjusted to 6.0 ± 0.1 and EC at 2.3 dS m^{-1} and was applied though an automated fertigation system consisting of drip irrigation with two emitters per container, dispensing 1 L·h^{-1} each. During the vegetative phase, three 2–h irrigations were applied per week while in the reproductive phase ~3.5 h irrigations were applied on a daily basis.

Leaching fraction (determined by measuring incremental additions of nutrient solution) was maintained at ~35% throughout the experiment. Plants were separated 45 cm between containers (from center to center) and 120 cm between rows of containers (3 plants m^{-2}) and trellised to one stem. The leaves were pruned periodically throughout the study period to maintain 11 to 13 mature leaves; trusses were also pruned to maintain five flowers per truss and 10 trusses were allowed to develop during the study.

2.3 Foliar and Drench Applications

Two foliar (40 and 100 days after sowing) or drench applications (1 and 100 days after sowing) were manually conducted with 100 mL of a NPs-ZnO solution at 1500 mg L^{-1}. NPs-ZnO solutions were previously dispersed with a sonicator (SONICS model VC505) during 15 minutes at 38% Abs. pH of the NPs-ZnO solutions was adjusted to 5.6 to 5.8 with H_2SO_4 prior applications.

2.4 Dry Weight, SPAD Index, Fruit Quality and Yield

Fruit firmness was measured with a penetrometer (AKSO model FT327, 8 mm tip) and the total soluble solids (SST) with a refractometer (ATAGO model ATC-1E) in three readings of fruits of the tenth truss. The total yield of tomato fruits was calculated by adding the weight of the fruits harvested from 10 trusses harvested during 77 d using a digital scale. The SPAD index was measured every 15 days, starting 30 days after sowing (SPAD-502 meter, Minolta, Japan). After the final fruit harvest, the plants were collected, bagged and placed in an oven at 70 ° C for 72 h (Novatech, model HS45-AIA, Murrieta, CA). The total dry weight of the plant (including pruned leaves, leaves, stem and roots) was recorded.

2.5 Gas Exchange Parameters

Photosynthetic rate, stomatal conductance, transpiration rate, and leaf temperature were measured with a portable photosynthesis system (LI-COR 6400XT, Biosciences, Lincoln, Nebraska) in leaves from the middle part of the plant. Measurements were conducted three times every 28 days between 11 am and 1 pm. The CO_2 concentration was 375.8 µmol mol^{-1}, the air temperature was 33.2 °C and the relative humidity was approximately 54.9% during the measurements.

2.6 Fruit Mineral Analysis

To determine the mineral composition of macronutrients (P, K, Ca, Mg, S) and micronutrients (Fe, Mn, Zn, Cu, Si), tomato fruit samples were dehydrated in a drying oven at 65°C for 48H (Novatech, model HS45-AIA, Murrieta, CA) and subsequently ground and sieved so that the powder was finally compressed into a tablet for reading. Finally, a wavelength X-ray fluorescence (WDXRF) spectrometer was used in measurements (BRUKER model S8 TIGER QUANT, Germany) using the QUANT-EXPRESS method.

2.7 Experimental Set Up and Statistical Analysis

The study consisted of two NPs morphologies: spherical or hexagonal (plus a control with no NPs-ZnO), two forms of NPs-ZnO application: foliar or drench, and with or without MDX-surface modification. The treatments were set in a randomized block three-factorial (3×2×2) design, resulting in a total of 12 treatments, 5 one-plant replicates per treatment. The statistical analysis was conducted with ANOVA and when significance was detected, a multiple mean comparison test was performed with Tukey`s procedure ($p<0.05$) using SAS 9.0.

3 Results

3.1 Effect of Nanoparticles Morphology

Hexagonal and spherical NPs increased total fruit yield, plant dry weight, leaf SPAD index, and fruit weight, firmness and soluble solids content (Table 1). Similarly, photosynthesis, transpiration rate and leaf conductance increased in plants treated with either hexagonal or spherical NPs, whereas leaf temperature increased only when spherical NPs were applied (Table 2). Fruit P, K and S increased when either hexagonal or spherical NPs were applied, whereas Mg increased only with hexagonal NPs (Table 3); fruit Ca was not affected by NPs morphology (Table 3). Micronutrients fruit concentration and Si increased in plants treated with either hexagonal or spherical NPs, except for Cu, which only increased with hexagonal NPs (Table 4). Plant dry weight and SPAD index were higher in plants treated with hexagonal compared to spherical NPs (Table 1), whereas photosynthesis rate and leaf temperature were higher in plants treated with spherical compared to hexagonal NPs (Table 2). Plants treated with hexagonal NPs showed higher fruit P, K (Table 3), Zn, Cu and Mn (Table 4) than those treated with spherical NPs, however, spherical NPs were associated with higher Fe concentration (Table 4).

3.2 Effect of Surface Modification of NPs with MDX

Surface modified NPs-ZnO with MDX resulted in increased fruit yield, fruit weight, plant dry weight and SPAD index compared to plants receiving non modified NPs (Table 1); however, fruit firmness and soluble solids was unaffected (Table 1). Photosynthesis, transpiration rate as well as leaf conductance were higher in plants treated with surface modified NPs (Table 2), although leaf temperature remained unaffected. Fruit P, K and Ca concentration was higher in plants treated with surface modified NPs-ZnO compared to plants receiving non modified NPs (Table 3), however, Mg and S were unaffected. Fruit Zn, Fe, Mn and Si concentration was higher in plants treated with surface modified NPs-ZnO compared to surface unmodified NPs (Table 4), however, Cu was unaffected.

3.3 Effect of the Form on which Nanoparticles were Applied

Drench applications of NPs resulted in higher fruit yield, SPAD index, fruit weight and firmness than plants with foliar applications (Table 1), however, plants dry weight and soluble solids were unaffected. Gas exchange parameters were not affected by the form of application (Table 2), however, fruit K (Table 3), Zn and Cu (Table 4) were higher when applications were by drench and fruit P with foliar applications (Table 3). Ca, Mg, S (Table 3), Fe, Mn and Si (Table 4) were unaffected by the form on which the NPs were applied.

3.4 Interactions on Agronomic Traits

The interaction between the morphology and surface modification with MDX showed that fruit yield was increased only when MDX was used with no NPs (Table 5), whereas the interaction between the morphology of the NPs-ZnO with the form on which they were applied shows that drenching was more effective in increasing fruit yield only when hexagonal NPs were used (Table 6). Total dry weight of plants was higher when the surface of NPs was modified with MDX when no NPs or when hexagonal NPs were used (Table 5). The applications of MDX without NPs (Table 5) and the application of the control treatment to the drench (Table 6) increased leaf SPAD index, while the NPs with surface-modified showed improved SPAD when applied by drenching (Table 7). MDX applied with no NPs (Table 5) and hexagonal NPs applied by drench (Table 6) enhanced the weight of fruits. Spherical NPs-ZnO with MDX resulted in increased fruit firmness compared to the control plants (Table 5). Soluble solids in fruits increased when MDX was applied with no NPS either by foliar (Table 8) or drench applications (Table 8), however, highest soluble solids were in fruits of plants treated with spherical NPs when surface was not modified with MDX (Table 8).

3.5 Interactions on Gas Exchange Parameters

MDX increased photosynthesis rate when applied with no NPs (Table 5); stomatal conductance, transpiration rate and leaf temperature (Table 5) exhibited similar trends, nonetheless, stomatal conductance was higher when hexagonal NPS were foliar applied (Table 6).

3.6 Interactions on Macronutrient Status

In general, the highest fruit P, K, Ca, Mg and S (Table 8) was obtained by plants treated with hexagonal NPs whose surface was modified with MDX and applied by drench. MDX applied with no NPs-ZnO increased fruit P and K concentration regardless if it was foliar or drench applied (Table 8). Fruit P was higher in plants treated with foliar applications of spherical or hexagonal NPs when their surface was not modified with MDX (Table 8); in contrast, fruit P was higher when spherical or hexagonal NPs were applied by drench (Table 8) and fruit K with hexagonal NPs applied by drench (Table 8).

No clear tendency was observed for fruit Ca and S concentration when NPs were foliar applied (Table 8) while Mg was decreased with surface-modified hexagonal NPs when they were foliar applied (Table 8). However, as for the other macronutrients, the highest Ca, Mg and S (Table 8), was observed in plants treated with surface modified hexagonal NPs applied by drench.

3.7 Interactions on Micronutrient Status

MDX applied with no NPs was associated with increased a fruit Zn, Fe, Mn and Si (Table 9) compared to plants without MDX and no NPs. MDX applied with no NPs-ZnO increased fruit Zn concentration regardless if they were foliar or drench applied (Table 9). Fruit Zn increased when spherical or hexagonal NPS were applied, but in general, spherical NPs were more effective in increasing Zn when their surface was modified with MDX, whereas hexagonal NPs were more effective when their surface was not modified (Table 9).

Highest fruit Fe was observed when the surface of hexagonal NPs was modified with MDX and applied by foliar sprays (Table 9), in contrast, Fe concentration was increased by either spherical or hexagonal NPs when their surface was not modified (Table 9). Highest fruit Mn was observed in plants treated with spherical NPs modified with MDX and applied by drench, however, when foliar applied MDX resulted in a decreased (Table 9). Fruit Si highest concentration occurred in plants treated with NPs whose surface was modified with MDX, however, spherical NPs were more effective when they were foliar applied, whereas hexagonal NPs were more effective when applied by drench (Table 9). Fruit Cu concentration was highest when hexagonal NPs whose surface was not modified with MDX were applied by drench (Table 9).

4 Discussion

Tomato plants increased growth, yield, fruit quality traits, gas exchange parameters, macronutrient (except for Ca), and micronutrient status when NPs-ZnO at 1500 ppm were applied, regardless of the morphology; these beneficial effects of NPs-ZnO have been ascribed to the properties of NPs, including their chemical composition, nanometric size (so that they may rapidly penetrate and distribute within the cell), increased surface area, stability and biochemical reactivity (Khodakovskaya et al. 2012). Similar findings were reported by Raliya et al. (2015) indicating that dry biomass in tomato increased when treated with NPs-ZnO at 100 ppm, and by Zhao et al. (2013b) reporting that the total dry biomass of cucumber increased by 10% compared to plants with no NPs applications.

The higher accumulation of macro and micronutrients observed in our study are in contrast to results reported by Zhao et al. (2014) indicating that NPs-ZnO at 400 and 800 ppm resulted in unaffected P, K, Ca, S and Fe, while that of Zn was increased, in cucumber fruits. In the present study, we are also reporting significant increase in fruit Zn concentration associated with NPs-ZnO applications, which is similar to the results reported by Song and Kim (2020) indicating that root and leaves Zn concentration increased when carrot (*Daucus carota* subsp. *sativus*) and lettuce plants were treated with 1000 ppm NPs-ZnO, while N concentration increased with 5 ppm in carrots and 5 to 20 ppm in lettuce (Song and Kim, 2020). In general, our results showed that NPs-ZnO resulted in increased content of macro (except for Ca and Mg) and micronutrients, which is contrast to reports by Nair and Chung (2017) indicating that there was a decrease in P, K, S and Cu, while Fe remained unaffected in Arabidopsis when NPs-ZnO was higher than 20 ppm.

The increase in fruit yield and quality parameters observed in our study was associated with an increase in all the gas exchange parameters, suggesting that both, NPs-ZnO (and MDX without NPs), promoted photosynthesis rate, which in turn was associated with an increased CO_2 diffusion as stomatal conductance, and consequently, transpiration rate was also increased. Ahmad et al. (2020) reported similar results in soybean treated with NPs-ZnO at 50 and 100 ppm, which may be because biomass and fruit yield are influenced by primary metabolic processes such as photosynthesis, respiration and transpiration which involve gas exchange with the surrounding environment (Taiz and Zeiger, 2006). The increase in the gas exchange parameters observed in this study are also in line with those reported in tomato treated with ZnO- NPs (8 ppm for 45 min) as there was a 50% increase in photosynthetic rate, 34% increased stomatal conductance, and 32% increased transpiration rate (Faizan et al. 2018); in wheat, chlorophyll concentration, photosynthesis, stomatal conductance and transpiration increased with the application of NPs-ZnO at 100 ppm (Hussain et al. 2018). The increased photosynthesis rate when NPs-ZnO were applied may be associated with the increased Zn concentration in plant tissues as suggested by Zn fruit content, which has been related to an increase in carbonic anhydrase activity, a Zn-metalloenzyme that catalizes CO_2 fixation (Faizan et al. 2020).

In our study, when considering the interaction between the morphology and MDX surface modification, the results indicate that they did not affect commercially-important plant responses as in both, hexagonal and spherical NPs, the plants exhibited unaffected yield and fruit quality. Nonetheless, MDX applied alone (with no NPs) impacted positively fruit productivity and some fruit quality traits as total fruit yield, fruit weight, firmness and total soluble solids were increased; in addition, plants resulted with higher total dry weight and leaves with a greener color as the SPAD index was increased. These responses were also associated with a higher photosynthesis and transpiration rate and leaf conductance and temperature. Fruit P, K, Zn, Fe, Mn and Si were also increased when MDX was applied with no NPs. MDX is a water-soluble polysaccharide and has the ability to protect from oxidation any encapsulated ingredient as well as to increase its stability and dispersion (Gu et al. 2012). Our results are in line with reports indicating that polysaccharides, such as MDX, play an important role in the absorption and transport of Zn in plants exposed to NPs-ZnO as demonstrated by Zhao et al. (2013a) because alginate, a polysaccharide, increased the release of Zn ions and promoted its bioaccumulation in plant tissues; in addition, our results indicate that MDX was associated with increased macro (except for Mg and S) and micronutrient status in the fruits, suggesting that this polysaccharide enhanced the uptake and transport of nutrients. MDX enhanced the effect of NPs-ZnO as they increased fruit Zn only when spherical NPs were foliar applied; Si and Cu exhibited similar trends. This is in agreement with reports by Zhao et al. (2012), Medina-Velo et al. (2017) and Wang et al. (2013) stating that MDX-modified NPs come into contact with root exudates (organic acids) causing NPs to dissolve in the roots, thus, increasing the release of ionic Zn and facilitating its transport to shoot. In wheat, urea coated with NPs-ZnO enhanced Zn accumulation, but N concentration was unaffected (Dimkpa et al. 2020).

Surface modification of NPs with MDX had a positive effect in increasing fruit macronutrients when hexagonal NPs were applied, while Zn, Fe and Cu decreased when applied by drench; this may be because NPs are transformed and dissolved in the roots and they are transported to the above-ground plant parts, for example, in mesquite (*Prosopis juliflora-velutina*) exposed to NPs-ZnO showed its presence in the root, while ionic Zn was detected in the rest of the plant organs (Hernández-Viezcas et al. 2011) this results were confirmed with a study performed with soybean (Priester et al 2012). Fruit Zn concentration was higher when no surface-modified hexagonal NPs-ZnO were applied by drench. This result is in contrast with reports by Raliya et al. (2015) in tomato indicating that NPs-ZnO at 250 ppm resulted in higher root and leaves Zn concentration when applications were sprayed to the leaves.

Averaged across all the other factors, the effect of NPs-ZnO was enhanced when applied by drench as yield, fruit weight and firmness were higher than those of plants that were treated with foliar applications, however, this increase was marginal (2.5%, 2.6% and 6.3%, respectively). Our results are in contrast to Su et al. (2019) that stated that foliar applications appear more effective in both NPs delivery and transport than drenching, and by Behboudi et al. (2018) reporting that the number of tillers in barley (*Hordeum vulgare* L.) was higher when chitosan NPs were foliar sprayed. However, in our study, both foliar and drench applications of spherical or hexagonal NPs resulted in increased yield, fruit weight, and SPAD index compared to control plants, suggesting that there is no effect of the application form. Nonetheless, foliar applications of hexagonal NPs resulted in decreased yield and fruit weight, which was partially restored when hexagonal NPs were applied by drench.

5 Conclusions

Nanoparticles of ZnO resulted in increased growth, yield and fruit quality traits; in general spherical or hexagonal NPs produced similar results. The morphology of the NPs, alone or combined with foliar or drench applications did not affect fruit yield or quality, however, hexagonal NPs increased biomass when their surface was modified with MDX. MDX applied alone increased yield and quality of fruits, although when combined with NPs morphology did not result in growth and yield improvement. In general, surface modification with MDX increased the nutrient status in fruits, except con Mg and S, and when surface modification was combined with spherical NPs there was an increase in fruit Zn, Si and Cu when they were foliar applied.

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Table 1 Response of the tomato crop to the application of different morphologies, modification and method of application of NPs-ZnO in fruit quality, dry weight and yield

	Yield (Kg/plant)	**Total dry weight** (g)	**SPAD index** (u SPAD)	**Weight of fruits** (g)	**Firmness** (Kg m2)	**TSS** (°Brix)
Morphology						
Control	7.3 b	347.7 c	54.3 c	146.7 b	3.1 b	5.8 b
Spherical	8.6 a	375.2 b	61.4 b	171.5 a	3.5 a	6.7 a
Hexagonal	8.5 a	407.9 a	64.6 a	169.4 a	3.3 a	6.5 a
ANOVA	*p≤ <.0001*	*p≤ <.0001*	*p≤ <.0001*	*p≤ <.0001*	*p≤ <.0001*	*p≤ <.0001*
MDX						
Non-Modified	7.9 b	364.1 b	58.6 b	157.3 b	3.2 a	6.2 a
Modified	8.4 a	389.8 a	61.6 a	167.8 a	3.3 a	6.5 a
ANOVA	*p≤ <.0001*	*p≤ 0.0005*	*p≤ <.0001*	*p≤ <.0001*	*p≤ 0.127*	*p≤ 0.0825*
Application method						
Foliar	8.0 b	371.6 a	59.4 b	160.6 b	3.2 b	6.4 a
Drench	8.2 a	382.3 a	60.8 a	164.3 a	3.4 a	6.3 a
ANOVA	*p≤ 0.0188*	*p≤ 0.1276*	*p≤ 0.0173*	*p≤ 0.0192*	*p≤ 0.0022*	*p≤ 0.724*
Interactions						
M*MDX	*p≤ <.0001*	*p≤ <.0001*	*p≤ <.0001*	*p≤ <.0001*	*p≤ 0.0001*	*p≤ <.0001*
M*A	*p≤ 0.0026*	*p≤ 0.0832*	*p≤ <.0001*	*p≤ 0.0025*	*p≤ 0.9084*	*p≤ 0.0984*
MDX*A	*p≤ 0.1144*	*p≤ 0.1284*	*p≤ 0.0008*	*p≤ 0.1145*	*p≤ 0.3864*	*p≤ 0.0101*
M*MDX*A	*p≤ 0.2679*	*p≤ 0.2593*	*p≤ 0.1834*	*p≤ 0.2768*	*p≤ 0.1488*	*p≤ 0.0005*

M=morphology, MDX=maltodextrin, A=application, TSS=total soluble solids. Different letters in same column are statistically different according to Tukey's multiple comparison test ($p< 0.05$)

Table 2 Response of the tomato crop to the application of different morphologies, modification and method of application of NPs-ZnO in physiological parameters

	Photosynthetic rate (µmol CO_2 $m^{-2}s^{-1}$)	**Stomatal conductance** (mol H_2O $m^{-2}s^{-1}$)	**Transpiration rate** (mmol H_2O $m^{-2}s^{-1}$)	**Temperature of leaf** (°C)
Morphology				
Control	12.75 c	0.316 b	8.21 b	31.20 b
Spherical	20.97 a	0.551 a	10.01 a	32.90 a
Hexagonal	17.88 b	0.562 a	10.02 a	31.81 b
ANOVA	*p≤ <.0001*	*p≤ <.0001*	*p≤ 0.0027*	*p≤ <.0001*
MDX				
Non-Modified	15.86 b	0.423 b	8.55 b	31.77 a
Modified	18.52 a	0.525 a	10.27 a	32.17 a
ANOVA	*p≤ 0.0082*	*p≤ 0.0006*	*p≤ 0.0006*	*p≤ 0.1636*
Application method				
Foliar	17.87 a	0.495 a	9.41 a	31.76 a
Drench	16.52 a	0.457 a	9.40 a	32.18 a
ANOVA	*p≤ 0.166*	*p≤ 0.162*	*p≤ 0.9916*	*p≤ 0.144*
Interactions				
M*MDX	*p≤ <.0001*	*p≤ <.0001*	*p≤ 0.0327*	*p≤ 0.0066*
M*A	*p≤ 0.9013*	*p≤ 0.0083*	*p≤ 0.4141*	*p≤ 0.7744*
MDX*A	*p≤ 0.2933*	*p≤ 0.0665*	*p≤ 0.2476*	*p≤ 0.4191*
M*MDX*A	*p≤ 0.1842*	*p≤ 0.6237*	*p≤ 0.3*	*p≤ 0.3022*

M=morphology, MDX=maltodextrin, A=application. Different letters in same column are statistically different according to Tukey's multiple comparison test ($p< 0.05$)

Table 3 Response of the tomato crop to the application of different morphologies, modification and method of application of NPs-ZnO in macroelement concentration

	P (mmol Kg)	**K** (mmol Kg)	**Ca** (mmol Kg)	**Mg** (mmol Kg)	**S** (mmol Kg)
Morphology					
Control	227.10 c	2565.01 c	127.66 a	45.94 b	108.65 b
Spherical	298.14 b	2799.45 b	143.67 a	47.65 ab	118.01 a
Hexagonal	312.94 a	2930.52 a	132.86 a	50.39 a	119.83 a
ANOVA	*p≤ <.0001*	*p≤ <.0001*	*p≤ 0.125*	*p≤ 0.0229*	*p≤ 0.0001*
MDX					
Non-Modified	254.19 b	2687.55 b	123.78 b	47.76 a	114.54 a
Modified	304.59 a	2842.43 a	145.68 a	48.22 a	116.45 a
ANOVA	*p≤ <.0001*	*p≤ <.0001*	*p≤ 0.002*	*p≤ 0.712*	*p≤ 0.3208*
Application method					
Foliar	287.02 a	2710.29 b	134.039 a	47.31 a	114.54 a
Drench	271.77 b	2819.69 a	135.427 a	48.68 a	116.45 a
ANOVA	*p≤ <.0001*	*p≤ <.0001*	*p≤ 0.826*	*p≤ 0.2743*	*p≤ 0.3208*
Interactions					
M*MDX	*p≤ <.0001*	*p≤ 0.0011*	*p≤ 0.5438*	*p≤ 0.1197*	*p≤ 0.1333*
M*A	*p≤ <.0001*	*p≤ 0.0009*	*p≤ 0.3788*	*p≤ 0.7336*	*p≤ 0.0995*
MDX*A	*p≤ <.0001*	*p≤ 0.0746*	*p≤ 0.0007*	*p≤ 0.0067*	*p≤ 0.1307*
M*MDX*A	*p≤ <.0001*	*p≤ 0.045*	*p≤ 0.0355*	*p≤ 0.0035*	*p≤ 0.0083*

M=morphology, MDX=maltodextrin, A=application. Different letters in same column are statistically different according to Tukey's multiple comparison test ($p < 0.05$)

Table 4 Response of the tomato crop to the application of different morphologies, modification and method of application of NPs-ZnO in microelement concentration

	Zn (µmol Kg)	Fe (µmol Kg)	Mn (µmol Kg)	Si (µmol Kg)	Cu (µmol Kg)
Morphology					
Control	3283.87 c	10704.3 c	2323.75 c	4.030 b	1803.6 b
Spherical	5946.92 b	16895.0 a	2657.45 b	5.061 a	2006.0 b
Hexagonal	6241.40 a	15507.3 b	3209.56 a	5.433 a	3157.6 a
ANOVA	*p≤ <.0001*	*p≤ <.0001*	*p≤ <.0001*	*p≤ <.0001*	*p≤ <.0001*
MDX					
Non-Modified	4834.02 b	13699.4 b	2568.46 b	4.5661 b	2581.34 a
Modified	5480.77 a	15038.3 a	2892.04 a	5.1167 a	2063.47 b
ANOVA	*p≤ <.0001*	*p≤ 0.0004*	*p≤ <.0001*	*p≤ 0.0009*	*p≤ <.0001*
Application method					
Foliar	5063.49 b	14362.9 a	2729.24 a	4.8711 a	2123.88 b
Drench	5251.31 a	14374.8 a	2731.26 a	4.8117 a	2520.94 a
ANOVA	*p≤ 0.0013*	*p≤ 0.9705*	*p≤ 0.9715*	*p≤ 0.6833*	*p≤ 0.0002*
Interactions					
M*MDX	*p≤ <.0001*	*p≤ <.0001*	*p≤ <.0001*	*p≤ 0.0132*	*p≤ <.0001*
M*A	*p≤ <.0001*	*p≤ 0.1019*	*p≤ 0.0064*	*p≤ 0.0724*	*p≤ 0.0005*
MDX*A	*p≤ 0.0014*	*p≤ 0.0023*	*p≤ <.0001*	*p≤ 0.4638*	*p≤ <.0001*
M*MDX*A	*p≤ <.0001*	*p≤ 0.0288*	*p≤ <.0001*	*p≤ <.0001*	*p≤ <.0001*

M=morphology, MDX=maltodextrin, A=application. Different letters in same column are statistically different according to Tukey's multiple comparison test ($p < 0.05$)

Table 5 Effect of the interaction of morphology and surface modification with MDX of NPs-ZnO on yield, fruit quality and gas exchange

M	**MDX**	**Yield** (Kg/plant)	**Total dry weight** (g)	**SPAD index**	**Weight of fruit** (g)	**Firmness** (Kgm2)	**Photo** (µmol CO_2 $m^{-2}s^{-1}$)	**Cond** (mol H_2O $m^{-2}s^{-1}$)	**Tran** (mmol H_2O $m^{-2}s^{-1}$)	**Temp** (°C)
C	Without	6.8 c	318.5 c	50.1 d	135.7 c	2.8 b	6.6 c	0.17 b	6.53 b	30.34 b
	With	7.9 b	376.9 b	58.4 c	157.6 b	3.3 a	18.9 ab	0.47 a	9.88 a	32.06 a
Sph	Without	8.5 a	386.9 b	61.8 bc	169.4 a	3.5 a	21.2 a	0.53 a	9.26 a	33.07 a
	With	8.7 a	363.4 b	61.0 c	173.7 a	3.5 a	20.8 ab	0.57 a	10.76 a	32.74 a
Hex	Without	8.3 a	386.7 b	63.9 ab	166.7 a	3.4 a	19.8 ab	0.58 a	9.87 a	31.92 a
	With	8.6 a	429.2 a	65.3 a	172.1 a	3.2 ab	15.9 b	0.54 a	10.16 a	31.71 ab

M=morphology, MDX=maltodextrin , Photo= photosynthetic rate, Cond=stomatal conductance, Tran=transpiration rate, Temp=temperature of leaf. Different letters in same column are statistically different according to Tukey's multiple comparison test ($p< 0.05$)

Table 6 Effect of the interaction of morphology and surface modification with MDX of NPs-ZnO on yield, leaf SPAD index, weight of fruit and stomatal conductance

M	**Application method**	**Yield** (Kg/plant)	**SPAD index**	**Weight of fruit** (g)	**Cond** (mol H_2O $m^{-2}s^{-1}$)
Control	Foliar	7.3 c	51.6 c	145.3 c	0.29 c
	Drench	7.4 c	57.1 b	148.0 c	0.34 c
Sph	Foliar	8.6 a	61.9 a	172.9 a	0.56 a
	Drench	8.5 ab	60.9 ab	170.2 ab	0.55 a
Hex	Foliar	8.2 b	64.7 a	164.1 b	0.64 a
	Drench	8.7 a	64.5 a	174.7 a	0.48 bc

M=morphology, MDX=maltodextrin, Cond=stomatal conductance. Different letters in same column are statistically different according to Tukey's multiple comparison test (p< 0.05)

Table 7 Effect of the interaction of MDX and application method of NPs-ZnO on leaf SPAD index

MDX	**Application method**	**SPAD index**
Without	Foliar	58.9 b
	Drench	58.3 b
With	Foliar	59.8 b
	Drench	63.4 a

MDX=maltodextrin. Different letters in same column are statistically different according to Tukey's multiple comparison test ($p < 0.05$)

Table 8 Effect of the interaction of morphology, surface modification with MDX and application method of NPs-ZnO on concentration macronutrients in tomato fruit

M	**MDX**	**TSS** (°Brix)		**P** (mmol Kg)		**K** (mmol Kg)		**Ca** (mmol Kg)		**Mg** (mmol Kg)		**S** (mmol Kg)	
		Foliar	Drench	Foliar	Drench	Foliar	Drench	Foliar	Drench	Foliar	Drench	Foliar	Drench
C	Without	5.56 cd	5.08 d	173.3 g	178.7 g	2404.1 dc	2450.9 d	113.9 c	113.9 c	43.9 c	43.9 c	105.0 b	105.0 b
	With	6.24 bc	6.48 bc	305.7 cd	250.8 e	2702.5 bc	2702.5 c	141.4 bc	141.4 bc	47.9 bc	47.9 bc	112.3 b	112.3 b
Sph	Without	6.32 bc	7.66 a	336.9 ab	227.1 f	2770.7 bc	2796.3 bc	158.9 ab	116.4 cd	47.9 bc	49.4 bc	118.5 ab	119.6 ab
	With	6.76 ab	6.10 cd	294.9 d	333.7 ab	2774.9 bc	2855.9 bc	137.3 bc	162.2 ab	45.3 c	47.9 bc	119.6 ab	114.4 ab
Hex	Without	6.34 bc	6.40 bc	316.4 bc	292.8 d	2787.7 bc	2915.6 b	133.1 bc	106.5 c	54.9 ab	46.6 bc	121.7 a	117.5 b
	With	6.98 ab	6.20 bc	294.9 d	347.6 a	2821.8 bc	3196.9 a	119.8 bc	172.2 a	43.9 c	56.2 a	110.2 b	129.9 a

M=morphology, MDX=maltodextrin,TSS=total soluble solids. Different letters in same column are statistically different according to Tukey's multiple comparison test (p< 0.05)

Table 9 Effect of the interaction of morphology, surface modification with MDX and application method of NPs-ZnO on concentration micronutrients in tomato fruit

		Zn (µmol Kg)		**Fe** (µmol Kg)		**Mn** (µmol Kg)		**Si** (µmol Kg)		**Cu** (µmol Kg)	
		Foliar	Drench	Foliar	Drench	Foliar	Drench	Foliar	Drench	Foliar	Drench
C	Without	2213.2 h	2014.2 h	8713.8 d	8713.8 d	1923.3 d	1923.3 d	3.6 e	3.6 e	1764.4 de	1764.4 de
	With	4324.1 g	4584.2 g	12694.7 c	12694.7 c	2724.2 c	2724.2 c	4.5 cd	4.5 cd	1844.7 de	1844.7 cd
Sph	Without	5043.1 f	6017.0 cd	17015.8 a	17200.8 a	3209.6 bc	2123.5 d	4.4 cde	5.9 ab	1588.3 e	2407.6 bc
	With	6266.9 cd	6460.7 bc	17636.5 a	15726.7 b	1856.6 d	3440.1 a	6.3 a	3.8 de	2187.3 cd	1841.1 de
Hex	Without	6685.1 bc	7031.8 a	13697.4 bc	16854.7 a	3373.4 ab	2857.7 bc	5.7 bc	4.3 de	2769.5 b	5198.0 a
	With	5848.8 de	5400.0 ef	16418.9 ab	15058.2 bc	3288.4 ab	3318.8 ab	4.9 cd	6.9 a	2591.1 bc	2071.9 de

M=morphology, MDX=maltodextrin. Different letters in same column are statistically different according to Tukey's multiple comparison test ($p < 0.05$)

CONCLUSIÓN GENERAL

La introducción de la nanotecnología dentro de la agricultura durante la última década establece que el desarrollo y aplicación de nanomateriales es un método efectivo para una agricultura de precisión que permite mejorar significativamente las producciones agrícolas del mundo y poder enfrentar la creciente demanda de alimentos de la población en constante expansión. Los objetivos de la aplicación de nanomateriales es la disminución de productos químicos usados convencionalmente para la producción agrícola, estos a través de nanofertilizantes o nanoplaguicidas que poseen liberación controlada, estabilidad y una entrega mejorada de los ingredientes activos. Estos nanomateriales han optimizado las dosis tradicionales de agroquímicos convencionales y no solo eso, sino que ha reducido costos de producción, aumentado los rendimientos agronómicos y minimizado la contaminación ambiental. Aún queda por investigar el potencial de la nanotecnología, la aceptación del consumidor, la seguridad y regulaciones gubernamentales, sin embargo, es evidente que este campo es muy prometedor y se espera mayor progreso en el futuro.