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Cultivo de frijol (*Phaseolus vulgaris* L.) acondicionado con nanopartículas de TiO_2: efecto en las comunidades microbianas de su rizósfera e implicaciones socio-ambientales

T E S I S

Que presenta

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“Esto también pasará…”

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INDICE DE CONTENIDOS

1. RESUMEN.

Los materiales con dimensiones nanométricas pueden ser diseñados y sintetizados con propiedades particulares para obtener ventajas competitivas, comparados con materiales similares de dimensiones mayores, su aplicación en la agricultura requiere considerar las implicaciones ambientales, sociales y económicas, e incluso tecnológicas, que podría tener su uso intensivo y extensivo particularmente cuando en México la nanotecnología se encuentra parcialmente regulada y donde la mayoría de las normas establecidas son de carácter voluntario. El efecto tóxico de algunos nano materiales ha sido ampliamente reportado. Sin embargo, también se han documentado los beneficios potenciales que tienen los materiales de dimensiones nanométricas cuando se aplican a los cultivos en dosis específicas. Mediante una extensa revisión documental, el presente trabajo pretende platear un enfoque prospectivo sobre el posible impacto de estas nuevas tecnologías agrícolas en aspectos socio-ambientales y adicionalmente de forma experimental se determinó el efecto de nanopartículas de dióxido de titanio ($nTiO_2$) en (fase cristalina anatasa) en la abundancia y diversidad de microorganismos de la rizósfera del cultivo de frijol (*Phaseolus vulgaris* L.) En el caso particular del experimento descrito en este estudio la aplicación de 150 o 300 mg de $nTiO_2$ por kilogramo de suelo (base seca) no afectó el desarrollo de las plantas de frijol, ni la estructura de la comunidad bacteriana suelo a granel, no rizosférico y rizosférico; sin embargo, el tiempo de exposición tuvo un efecto significativo en la abundancia de las comunidades bacterianas. Se deben realizar pruebas específicas para cada condición y particularidad con respecto al efecto de los nanomateriales de ingeniería en los cultivos y su impacto en la salud humana y ambiental. El efecto de los nanomateriales sobre los cultivos está en función del tipo de material, la dosis aplicada, la vía de administración, el tiempo de contacto nanomaterial-planta, la carga superficial, la etapa fenológica del cultivo, el tipo de cultivo y la presencia, ausencia y tipo de cubierta que tenga el nanomaterial.

2. ABSTRACT

Materials with nanometric dimensions can be designed and synthesized with particular properties to obtain competitive advantages, compared with similar materials of larger dimensions, their application in agriculture requires considering the environmental, social and economic, and even technological implications that could have their use intensive and extensive particularly when in Mexico nanotechnology is partially regulated and most of the established norms are voluntary. The toxic effect of some nanometric structures has been widely reported. However, the potential benefits of materials of nanometric dimensions when applied to crops in specific doses have also been documented. Through an extensive documentary review, the present document intends to focus a prospective approach on the possible impact of these new agricultural technologies in socio-environmental aspects and additionally determined experimentally the effect of titanium dioxide ($nTiO_2$) nanoparticles in (crystalline phase anatase) in the abundance and diversity of microorganisms of the rhizosphere of the bean crop (*Phaseolus vulgaris* L.) In the particular case of the experiment described in this study the application of 150 or 300 mg of $nTiO_2$ per kilogram of soil (dry base) did not affect the development of bean plants, nor the structure of the bulk, non-rhizospheric and rhizospheric bacterial community; However, the exposure time had a significant effect on the abundance of bacterial communities. Specific tests must be carried out for each condition and particularity with respect to the effect of engineering nanomaterials on crops and their impact on human and environmental health. The effect of nanomaterials on crops depends on the type of material, the dose applied, the route of administration, the nanomaterial-plant contact time, the surface load, the phenological stage of the crop, the type of crop and the presence, absence or specific characteristics of the nanomaterial coating.

3. INTRODUCCIÓN

La necesidad de producir alimentos para una población mundial en aumento, ha llevado a los investigadores en ciencias agrícolas del siglo XI a desarrollar alternativas tecnológicas que no solo sirvan para mejorar la calidad y rendimientos productivos, si no para que esto se lleve a cabo sin afectar los agroecosistemas (Bharadwaj, 2016). Hoy en día se plantea la necesidad de lograr dichos objetivos con un enfoque sustentable. Se estima que se requiere incrementar alrededor de un 70-100% la producción de alimentos hacia el 2050, sin embargo, la actividad agrícola actual reporta pérdidas en los cultivos ocasionados por la presencia de plagas de insectos, enfermedades y maleza, las cuales ascienden anualmente a 248 000 millones de dólares a nivel global (Fried et al., 2017). La protección de cultivos y el aumento de la productividad implica el uso indiscriminado de agroquímicos (plaguicidas, herbicidas y fertilizantes) lo cual esta ocasionando el deterioro gradual del suelo, de los agro-ecosistemas, así como la generación de residuos que contaminan el ambiente. La investigación en nanotecnología en los últimos años se ha presentado como una alternativa sustentable, que puede transformar el sector agrícola, el desarrollo de dispositivos de detección de enfermedades y de deficiencias nutricionales (nanosensores), de sustratos para retener humedad y la encapsulación de nutrientes en materiales de lenta liberación son algunos de los ejemplos. Se ha estudiado incluso la posibilidad de mejorar la calidad nutricional de algunos alimentos (Khot et al., 2012; Nuruzzaman et al., 2016; Fraceto et al., 2016).

Sin embargo, existen consideraciones socio ambientales que no deben dejarse de lado, si bien la nanotecnología ofrece igualmente alternativas para la recuperación de agua, aire y suelo contaminado con residuos de origen diverso, quedan muchas dudas aun sobre el uso masivo de los nanomateriales dado que eventualmente también se convertirán en residuos. En los últimos veinte años diversos autores han hecho estudios para documentar los posibles efectos sobre plantas de importancia comercial de la aplicación de gran cantidad de compuestos de dimensión nanométrica, el problema es que no hay consenso posiblemente debido a la gran diversidad de factores que condicionan la respuesta. La necesidad de más investigación y desarrollo en agronanobiotecnología para la seguridad alimentaria será necesaria en los próximos años, algunas preguntas están aún sin ser contestadas para su uso en la agricultura, específicamente en términos de toxicidad; ya que podrían afectar la salud de las personas y el medio ambiente (Handford et al., 2014). Por lo antes expuesto, el objetivo de este trabajo fue en primer lugar experimentalmente contribuir a la documentación de los efectos de la aplicación de nanomateriales en plantas de frijol (nanopartículas de óxido de zinc, óxido de hierro, y dióxido de titanio) y por otra parte documentar los efectos de dióxido de titanio de dimensiones nanometricas (nanopartículas de TiO_2 en fase cristalina anatasa por tratarse de uno de los compuestos más utilizados en la industria en la actualidad) sobre las comunidades bacterianas de la rizósfera de plantas de frijol común, (siendo un aspecto poco abordado) mediante la producción de artículos originales. En segundo lugar, realizar una extensa revisión cuyo propósito es mostrar y poner en el contexto global actual las aplicaciones potenciales que ofrece la nanotecnología para el control de plagas y enfermedades, así como para la generación de nuevos agronano insumos que incrementen la producción de alimentos y que ayuden a reducir el impacto ambiental de los agroinsumos sintéticos tradicionales; dicha revisión se presenta en diversos documentos cuyo propósito principal es la de difundir los conocimientos actuales generados por la comunidad científica durante los últimos veinte años, adicionalmente se plantea la situación actual de México y la nanotecnología agrícola, y una aproximación al desarrollo de una política pública que sirva para regular el uso de nanoinsumos, y finalmente se presenta un análisis de la investigación global en nanotecnología y agricultura, así como la configuración actual de los grupos de investigación en el área; cuya interacción y colaboración explicará el desarrollo de patentes y el posicionamiento de algunos países en investigación y desarrollo de la nanobiotecnologia agrícola en los próximo años.

4. ESTADO DEL ARTE

4.1 La agricultura en México

México tiene un territorio de 198 millones de hectáreas, de las cuales cerca de 30 millones son suelo de uso agrícola que participa con el 3.1% del producto interno bruto (INEGI, 2016). La agricultura es un sector importante por sus funciones en el desarrollo económico, social y ambiental del país. En México la agricultura emplea 13% de la población y cerca de 24% de los mexicanos vive en zonas rurales, amenazados por temas de migración y cambio de uso de suelo. A pesar de que la actividad agrícola mexicana está crecimiento, esta se encuentra fuertemente influenciada por temporalidades propias de la actividad agrícola, sujeta a la oferta-demanda de productos y amenazada por las relaciones comerciales actuales con Estados Unidos de Norteamérica, que podrían afectar los volúmenes de exportación y los costos de insumos. Es necesario incrementar la producción de alimentos a través de mejores políticas públicas, capacitación, semillas mejoradas, educación, etc. Sin embargo, los avances científicos y tecnológicos serán los factores más importantes que definirán el abasto de alimentos innocuos y asequibles y, la autosuficiencia alimentaria de México. Para lo anterior se requiere obtener nuevos conocimientos que logren transformar el sistema alimentario tradicional en un sistema alimentario sustentable, para que los mexicanos se alimenten con productos nacionales, innocuos y asequibles. La combinación de áreas de conocimiento como biotecnología, ecología y agronomía, con tecnologías como la nanotecnología y la ingeniería genética (clonación, organismos genéticamente modificados, etc.) podría ser una herramienta muy útil para optimizar e impulsar el sector primario.

4.2 La nanotecnología y la agricultura

La nanotecnología se enfoca en el estudio y diseño de materiales a escala nanométrica (1 a 100 nanómetros) que producen complejos sistemas en los que se modifican algunas características específicas (Bawa et al., 2005). Durante los últimos años, el desarrollo de nuevos productos es una prioridad científica y tecnológica para muchos países (León-Silva et al., 2016) y esto se debe a las propiedades novedosas de las nanopartículas: mayor superficie de reacción por volumen, capacidad de intercambio catiónico, complejación, mayor reactividad, estructura inusual, mayor estabilidad, forma, agregación y relación de adsorción de iones (Carrillo González et al., 2015; Nel et al., 2006; Sharon et al., 2010), que difieren completamente de su forma original de moléculas y materiales a granel (Guo, 2004; Li et al., 2001). Los nanomateriales se han desarrollado en varios campos de la industria, medicina, electrónica, energética, genética, aeronáutica, entre otros.

Una de las áreas más importantes y prioritarias es la agricultura, debido a que más del 60% de la población de los países en desarrollo depende de ella para su sustento (Brock et al., 2011). La FAO público en 2013, información sobre el estado del arte de la nanotecnología en alimentos y agricultura, en su reporte documentó investigaciones llevadas a cabo durante 10 años, enfocadas hacia la sustentabilidad y soluciones a los problemas ambientales. Estas investigaciones se centran en: la liberación de ingredientes activos (manejo de enfermedades y protección de cultivos), minimizar la pérdida de la fertilización y aumentar el rendimiento, así como la producción de bionano compuestos de cultivos tradicionales (Parisi et al., 2014). Los informes de dichas investigaciones sobre posibles aplicaciones en la agricultura han sido tanto positivos como negativos. Sin embargo, existen reportes en los que se han encontrado resultados favorables, por ejemplo, en el caso de la fertilización, germinación y promotores del crecimiento, sensores de contaminantes y otras sustancias y, recuperación y tratamiento de suelo y agua (Han 2007, Stoimenov et al., 2002). Nuestro conocimiento sobre las interacciones de las nanopartículas de uso agrícola con el medio ambiente aun es limitado y debido a la complejidad que representa, todavía hay un largo camino para entenderlo completamente. La ONU en 2013, planteó la necesidad de aumentar la producción de alimentos, ya que para el 2050 se calcula que habrá una población de 9100 millones de personas. Existe actualmente una tendencia hacia a la producción de cultivos energéticos, derivado de los esfuerzos para la mitigación del cambio climático, y por la reducción inminente de las reservas de hidrocarburos. Al mismo tiempo, en el foro de expertos organizado en 2009 por FAO “Como alimentar al mundo en 2050" se planteó que será necesario aumentar la producción de cereales 70% para 2050. La nanotecnología podría suministrar herramientas a la agricultura moderna e incluso ser útil en la solución de los problemas futuros relacionados con la producción de alimentos y la demanda energética con un enfoque sustentable. Sin embargo, se ha demostrado que algunas NP afectan el desarrollo y rendimientos de los cultivos agrícolas (Lin and Xing 2008, Asli and Neumann 2009; Adhikari et al., 2012; Dimpka et al., 2012; Shaw and Hossain 2013; Pradhan et al., 2015). Hoy en día, los investigadores buscan alternativas sustentables y menos agresivas para controlar las plagas, enfermedades, degradar contaminantes y nutrir los cultivos, enfrentando recursos limitados como el agua, el suelo y los nutrientes. Por consiguiente, las inversiones e innovación en nanotecnología aplicadas a la protección de cultivos podrían ser una gran contribución a este esfuerzo. La aplicación de herramientas de biotecnología, cuyas nuevas técnicas en genética, agricultura de precisión, cultivos de tejidos específicos, más el desarrollo actual de la nanobiotecnología especializada en biología molecular y celular, podría ayudar a comprender la respuesta biológica de cultivos importantes y la interacción con los nanocompuestos. Lo anterior implicaría mejorar diversas propiedades de los cultivos como los rendimientos, los valores nutricionales, la absorción de nutrientes y varios agroquímicos, entre otras (Prasad et al., 2010; Tarafdar et al., 2013).

Dependiendo de su naturaleza, tamaño, forma, agregación, dosis, estado de la planta o del suelo, y la forma de aplicación de nanopartículas, estas pueden tener diferentes funcionalidades, beneficios e incluso toxicidad en los sistemas de las plantas (Lee et al., 2008; Lin y Xing, 2008; Raliya et al., 2016; Seeger et al., 2009; Sunada et al., 2008). Se han documentado el empleo de algunas nanopartículas para promover efectos adversos en microorganismos; (Chen y Chiang, 2008; Singh y Nalwa, 2011) o aprovechando su actividad antifúngica (Kumari y Yadav, 2014), por lo que son útiles en el control de plagas y enfermedades de cultivos.

Las aplicaciones de la nanotecnología en la protección de cultivos son diversas, pero se centran principalmente en la elaboración de agroquímicos encapsulados de liberación lenta. Se han desarrollado nuevos nanomateriales basados en el uso de nanopartículas metálicas, poliméricas e inorgánicas que se aplican para mejorar los nanosistemas inteligentes con la capacidad de capturar e inmovilizar nutrientes y su liberación gradual en el suelo para aumentar la eficiencia del fertilizante. Además, el desarrollo de nanosensores permite detectar la presencia de plagas y enfermedades en los cultivos (Dubey y Mailapalli, 2016; Fraceto et al., 2016) y se pueden utilizar varios tipos de nanopartículas metálicas como Ag, Fe, Cu, Zn. con un enfoque dual, ya sea como nanofertilizantes, al tiempo que mejora la germinación de las semillas y al promover el crecimiento de las plantas, entonces podrían usarse contra algunos microorganismos patógenos y plagas (Le Van et al., 2016).

Cabe destacar que la evaluación y aplicación de nanomateriales en agricultura, investigar el comportamiento de los suelos resultado de las interacciones podrían ser de gran valor para reducir la actual escasez mundial de alimentos sin restar importancia a la posible toxicidad de las mismas al entrar en cadenas tróficas en los cultivos y su impacto en la salud humana y ambiental considerando como destino final de las nanopartículas como contaminantes. El objetivo de este trabajo fue estudiar el efecto de $nTiO_2$ en i) el desarrollo de las plantas de frijol, ii) la comunidad bacteriana en el suelo cultivado con plantas de frijol común (*Phaseolus vulgaris* L.), iii) las comunidades bacterianas en la rizosfera y iv) una extensa revisión de los aspectos importantes de las tendencias actuales de la aplicación de nanopartículas en la producción agrícola.

4.3 Nanotecnología y el cuidado del ambiente

El sistema alimentario actual a nivel mundial no es sustentable y por décadas ha causado daños ambientales, entre ellos las emisiones de gases de efecto invernadero, el uso irracional de agua potable, la contaminación de suelos y mantos acuíferos por el nitrógeno y fósforo, el uso de pesticidas, etc.

Sin embargo, las investigaciones recientes en materia de nanotecnología ambiental demuestran que esta puede ser una herramienta útil para reducir la contaminación del medio ambiente. Peters et al. (2016), desarrollaron nanoencapsulados y nanocompuestos para alimentos y aditivos para piensos, biocidas, plaguicidas y materiales en contacto con alimentos. También Ibrahim et al. (2016), aplicaron nanomateriales como catalizadores en procesos de fitorremediación y el uso de estabilizadores para mejorar su rendimiento.

Por otra parte, la nanotecnología también ofrece alternativas para la recuperación de agua y suelos. Ejemplos del uso de nano productos en ciencias ambientales son los reportados por Ali et al. (2016), quienes aplicaron nanomateriales para la degradación fotocatalítica de contaminantes orgánicos; Scognamiglio et al. (2016), emplearon nanosensores para el mismo fin. Elango y Roopan (2016), usaron nanomateriales para la degradación del azul de metileno; Begum et al. (2016) emplearon nanosensores para la detección rápida de estímulos ambientales como pH, fuerza de iones y moléculas biológicas; Pereira et al. (2015), utilizaron microorganismos para biosíntetizan nanopartículas metálicas y Bogdan et al. (2015) crearon nanomateriales con superficies autodesinfectantes.

4.4 La nanotecnología en México

En México la nanotecnología es incipiente; con base en Foladori (2011), la presencia de las nanotecnologías creció y se extendió por toda América Latina durante la primera década del siglo XXI. Las políticas de ciencia y tecnología han desempeñado un papel importante en el desarrollo de estas nuevas tecnologías. Diversas instituciones internacionales, como el Banco Mundial (BM), la Organización para la Cooperación y el Desarrollo Económico (OCDE) y la Organización de los Estados Americanos (OEA) promovieron políticas similares de ciencia y tecnología e incluyeron la nanotecnología como un área prioritaria. De acuerdo con Foladori y Zayago (2010), en México no existe discusión del impacto de la nanotecnología sobre aspectos sociales, legales, laborales, de salud y medio ambiente.

De acuerdo a Zayago (2011) la política mexicana en ciencia y tecnología (CyT) se ha intentado coordinar con el sector empresarial, aunque los esquemas han variado en cada sexenio. El Estado intentó vincular la CyT con la producción y el consumo en un principio, pero en los últimos años éste ha compartido la responsabilidad con empresas, universidades y centros de investigación, y ha utilizado al mercado para transferir a la sociedad los posibles beneficios tecnológicos.

Las prioridades del sector Ciencia, Tecnología e Innovación deben incluir temas relevantes de la agenda internacional como la biotecnología, la nanotecnología y los materiales (PECITI, 2008). Sin embargo, el actual Programa Especial de Ciencia y Tecnología 2014-2018 tiene como tema prioritario en Desarrollo Tecnológico el área de nanomateriales y de nanotecnología (PECITI, 2014) y no menciona de qué forma o en qué sentido dirigir esos temas; mientras que en el mismo programa en el área de Sociedad habla de combate a la pobreza y seguridad alimentaria (Zayago, 2011). Es decir, a pesar de que el Programa Especial de Ciencia y Tecnología 2014-2018 no vincula a la nanotecnología con el combate a la pobreza y la seguridad alimentaria, sí los considera temas prioritarios.

4.5 El cultivo de frijol, importancia ecológica de las leguminosas.

Con base en el reporte agroalimentario de FIRA para el año 2016, el frijol ha tenido una tendencia positiva durante los últimos diez años, incremento que se justifica debido al aumento de los rendimientos por unidad de área. México se encuentra entre los seis países que producen el 63% de la cosecha mundial, junto con Brasil, China, Estados Unidos, Myanmar y Tanzania. Al mismo tiempo, México es uno de los principales consumidores de esta leguminosa, que ocupa el cuarto lugar en importancia después de maíz, pastos y sorgo. Al 2015, la producción de frijol ascendió a 969.1 miles de toneladas, la mayoría bajo régimen de temporal. En 2015 la balanza comercial de este producto fue deficitaria, por lo que se importaron 88 543 toneladas, el 5% del consumo aparente de frijol en México.

El frijol es un cultivo domesticado en América aproximadamente hace 8,000 años (Bitochi et al., 2013). Su relevancia alimenticia reside en su contenido proteico (20-25%), similar a otras leguminosas como la soya y el cacahuate. En nuestro país representa el 36% de la ingesta de proteínas con la sola desventaja de que en sus proteínas están poco presentes los aminoácidos azufrados (Singh et al., 1999).

Las raíces de las leguminosas forman asociaciones simbióticas con diversos géneros de bacterias del suelo denominados colectivamente rizobias. El resultando de esa asociación simbiótica es la formación de órgano denominado nódulo, en el que se da la fijación biológica de nitrógeno (FBN) la cual tiene importancia ecológica, en términos de abundancia y diversidad de especies y en términos de disminución de uso de fertilizantes químicos. Más de 18 000 especies de leguminosas interactúan con bacterias para realizar la FBN y fijar la cuarta parte del nitrógeno fijado en la biosfera. Cuando se convierte el nitrógeno atmosférico (N≡N) en amonio (NH_4), se mejora el crecimiento de la planta asociada, ya que el N≡N se convierte en una forma asimilable (NH_4) para la planta, dándose de modo natural una fertilización. Se estima que a través de esta fertilización de suelo por dicha interacción simbiótica se incorporan de 60 a 120 kg de nitrógeno por hectárea.

4.6 Efectos de las nanopartículas de dióxido de titanio en plantas e interacciones con el suelo

El dióxido de titanio se aplica ampliamente en la industria, se ha utilizado en productos como pinturas, colorantes, cosméticos de plástico, productos de limpieza y cuidado personal como pasta de dientes y protector solar (Fan et al., 2013; Jacobs et al., 2010). Los polvos de dióxido de titanio se han sintetizado durante los últimos 100 años, a partir de la ilmenita mineral ($FeTiO_3$), es un compuesto tecnológico atractivo debido a sus propiedades de dispersión de luz (confiere turbidez y apariencia blanquecina) y bajo costo, también es un material semiconductor que exhibe actividad fotocatalítica en presencia de luz. TiO_2 es un aditivo permitido y registrado por la FDA (E171) clasificado como seguro y "biológicamente inerte" (humanos y animales) (Rodriguez-Escamilla et al., 2019). La dispersión de la luz y las propiedades de índice de refracción dependen directamente del tamaño de partícula, en los últimos años estas características canalizaron la producción de partículas más pequeñas como el desarrollo de partículas de dióxido de titanio micronano y nanoescalado. En los EE. UU., la producción de $nTiO_2$ podría alcanzar los 2.5 millones de toneladas para 2025 (Robichaud et al., 2009). Las nanopartículas de TiO_2 podrían afectar las plantas y los organismos del suelo, y se ha convertido en una gran preocupación debido a sus efectos de toxicidad mal documentados. Los últimos estudios sobre el comportamiento de $nTiO_2$ mostraron que causan efectos a través de la activación del estrés oxidativo al producir daño celular, y también la activación de varios mecanismos de defensa, como la respuesta inmune o la inflamación en células de mamíferos (Iavicoli et al., 2011). El titanio interactúa estrechamente con las plantas porque es el segundo metal de transición más abundante que se encuentra en la corteza terrestre (aproximadamente 6.320 ppm) (Feizi et al., 2013). Se han informado efectos positivos y negativos de los compuestos de titanio en diferentes cultivos, incluido el aumento de otros elementos en el tejido vegetal, los efectos sobre la actividad enzimática y el aumento de otros metabolitos como la clorofila. A ciertas concentraciones, los NP de TiO_2, Ag, Fe_3O_4, ZnO y SiO_2 alteran favorablemente las respuestas fisiológicas como la germinación, la actividad antioxidante y enzimática, la síntesis de clorofila y el crecimiento de diferentes plantas (Lu et al., 2002, Bao-shan et al., 2004, Zheng et al., 2005, Gao et al., 2008; Pandey et al., 2010; Feizi et al., 2012, Suriyaprabha et al., 2012, Wang et al., 2013. La actividad biológica y la biocinética de las nanopartículas depende de parámetros como el tamaño, la forma, la química, la cristalinidad, las propiedades de la superficie (área, porosidad, carga, modificaciones de la superficie, revestimiento), estado de aglomeración, biopersistencia y dosis (Casals et al., 2008). Otros autores informaron que estaban negativos o ausentes efectos; Asli y Neumann (2009) encontraron que $nTiO_2$ inhibe el crecimiento foliar y la transpiración, así como el desarrollo de la raíz que afecta el sistema de transporte en las plántulas de maíz. Contrariamente, Boonyanitipong et al. (2011) aplicaron $nTiO_2$ germinado a semillas de arroz germinadas (*Oryza sativa* L.) y no encontró ningún efecto en longitud de la raíz.

Las nanopartículas de TiO_2 podrían tener efectos sobre los organismos vivos del suelo, como las plantas y los microorganismos. Se ha informado que la acumulación de ciertas nanopartículas (NP) en el suelo modifica la actividad, diversidad, abundancia y crecimiento de sus microorganismos (León-Silva et al., 2016; Zhai et al., 2016; Samarajeewa et al., 2017)

Parece no haber consenso con respecto a la reacción de las plantas a $nTiO_2$, pero hasta hoy se sabe que la reactividad de las nanopartículas (NP) depende del tipo, forma (Raliya et al., 2016) peso, tamaño, agregación y tamaño dependiente sedimentación o difusión hacia la célula, condiciones del suelo, dosis y método de aplicación y condiciones de las plantas (Lin y Xing, 2008; Lee et al., 2008; Sunada et al., 2008, Seeger et al., 2009). A ciertas concentraciones, los NP de TiO_2, Ag, Fe_3O_4, ZnO y SiO_2 alteran favorablemente las respuestas fisiológicas como la germinación, la actividad antioxidante y enzimática, la síntesis de clorofila y el crecimiento de diferentes plantas ((Lu et al., 2002, Bao-shan et al. , 2004, Zheng et al., 2005, Gao et al., 2008; Pandey et al., 2010; Wang et al. 2011, Feizi et al., 2012, Suriyaprabha et al., 2012, Wang et al., 2013) Acerca de los cambios reportados en las raíces; Bao-shan et al. (2004) aplicaron nano-SiO_2 en plántulas de *Larix olgensis* y encontraron que $nSiO_2$ mejoró la longitud de la raíz; altura media, diámetro del collar de la raíz, número de raíces laterales. $nTiO_2$ no afectó el alargamiento de la raíz de colza, trigo y arabidopsis pepino, lechuga y rábano ((Larue et al., 2011; Tang et al., 2012). Asli y Neumann 2009 encontraron que $nTiO_2$ inhibe el crecimiento y la transpiración de las hojas al dañar el mecanismo de transporte de agua de la raíz de plántulas de maíz. Contrariamente, Boonyanitipong et al. (2011) aplicaron $nTiO_2$ a semillas de arroz, *Oryza sativa* L., y no encontraron efecto en la longitud de la raíz.

La relación entre plantas y microorganismos bajo el efecto de TiO_2 está poco documentada. Priester et al. (2012) observaron que CeO_2 afectó el crecimiento y la fijación de nitrógeno de los nódulos bacterianos de las raíces de la soja. Dimka et al 2015, usaron nZnO y probaron la interacción de *Phaseolus vulgaris* L. bajo la presencia de la nanopartícula, informaron una respuesta positiva, la actividad de la reductasa férrica de la raíz se redujo un 31% en plantas expuestas a NP, lo que sugiere una contribución nano específica de ZnO, adicionalmente no hubo cambios significativos en la población de *Pseudomonas chlororaphis* O6. Fan et al. (2014) estudiaron la simbiosis entre rizobios y leguminosas en guisantes de jardín expuestos a $nTiO_2$. Encontraron resultados similares a los de otros autores sobre las respuestas fisiológicas. Pero también usaron *R. leguminosarum* bv. Viciae 3841, un compañero rizobial común, y fue afectado por $nTiO_2$, mostrando cambios morfológicos en las células bacterianas, y el desarrollo del nódulo de la raíz y la composición del nódulo de la pared del polisacárido con el posterior retraso en la fijación de nitrógeno.

Ge et al. (2011) informaron los efectos de $nTiO_2$ en la abundancia y diversidad de comunidades bacterianas en el suelo de los pastizales, y en una segunda palabra, Ge et al. (2012), encontraron que el número de taxones bacterianos con disminución de la abundancia relativa fue mayor que el número de taxones que aumentaron. Entre los taxones con abundancia relativa disminuida estaban las bacterias potencialmente involucradas en la fijación de N_2 y la oxidación de metano, mientras que entre las que aumentaron estaban las bacterias potencialmente involucradas en la mineralización de compuestos orgánicos refractarios.

4.7 La necesidad de medir los efectos socio-ambientales de la aplicación de nanopartículas de titanio en cultivo de frijol

La producción y aplicación de nanopartículas tiene relevancia por tres razones: Por los beneficios que aportan en distintas áreas, por ser una tecnología de reciente aparición y que se encuentra en pleno desarrollo y por los riesgos asociados a ellas. Existen actualmente una tendencia hacia la conciencia ecológica por lo que aumentar las bases de datos sobre los efectos que podrían tener las nanopartículas sobre el ambiente representa una prioridad dado que se ha estimado que en 2010 se liberaron entre 260000 y 390000 toneladas de materiales nanoestructurados, los cuales terminaron en rellenos (63-91%), suelos (8-28%), cuerpos de agua (0,4-7%) y en la atmósfera (0,1-1,5%) (3). Se sabe poco acerca de cómo se comportan en distintos ambientes y de los efectos que tienen sobre los seres vivos (GEO YEAR BOOK, 2007). En los próximos años la nanotecnología trascenderá en aplicaciones en diversas áreas tecnológicas y científicas, sin embargo, aún no existe una reglamentación específica para su aplicación masiva. Con respecto a la producción agrícola, por un lado, se experimenta la nanoestructuración de todo tipo de agroquímicos (fertilizantes, herbicidas y pesticidas, entre otros). Por otro lado, también se avanza en el diseño de materiales funcionales para aplicaciones puntuales tales como sistemas de irrigación, plásticos inteligentes, para embalaje, entre otros. Estudios recientes han demostrado el hecho de que las nanoparticulas podrían ser bioacumuladas y bioamplificadas en una cadena alimenticia terrestre (Judy et al., 2011). Se han propuesto modelos prácticos cuantitativos para estudiar el comportamiento de las Nanopartículas en general en los sistemas acuáticos y su impacto en los organismos acuáticos (Quik, 2013). Haciendo énfasis en el suelo como sistema ecológico las posibles ventajas de las aplicaciones de los materiales nanoestructurados en la agricultura, como el empleo de nano-fertilizantes y el mejoramiento de los pesticidas con la incorporación de Nanopartículas metálicas. Además, resume la función de los principales organismos en el mantenimiento de la salud del suelo para la agricultura. Entre las ventajas consideraras por diversos autores se encuentran: Hacer más eficientes productos ya conocidos, que los productos desarrollados tengan múltiples aplicaciones, y una de las más importantes; lograr la reducción y sustitución del uso de materiales. Sin embargo, algunos aspectos son aun debilidades: 1) Propiedades toxicológicas desconocidas de los nanomaeriales; 2) posibles afectaciones a la salud, y 3) posibles afectaciones a la situación del empleo y la división social del trabajo). Por otro lado, no se han documentado los efectos a largo plazo del uso de nanopartículas. Cada nanoparticula tiene un comportamiento particular sus propiedades son únicas y en consecuencia la toxicidad será diferente. Existe el término "nanotoxicidad" para referirse a los efectos adversos que las Nanopartículas manufacturadas tienen sobre los organismos vivos y los ecosistemas, es un hecho que los organismos no tienen un sistema de purificación o de inmunidad para responder a la exposición a las nanopartículas diseñadas por el hombre. Se ha señalado que

Nanopartículas de 12 nm pueden atravesar la barrera sangre-cerebro y que Nanopartículas de 30 nm o menos, pueden ser endocitadas por las células (Alkilany & Murphy, 2010).

Se plantean las siguientes preguntas: ¿Cómo las Nanopartículas cambian en el tiempo una vez que están presentes en el ambiente? ¿Qué efectos podrían tener en los organismos?, y ¿Qué efectos podrían tener en los ecosistemas?

Por otro lado, la Nanoética incluye preguntas qué pueden ser dirigidas a la creación de políticas públicas: ¿Cuáles son los riesgos potenciales a la seguridad y la salud con las aplicaciones de la Nanotecnología? ¿Quién es responsable si algo pasa? ¿Cuáles son los derechos de un individuo afectado por un proceso o producto de la Nanotecnología? ¿Cómo se puede proteger a la sociedad de los riesgos de la Nanotecnología?

5. JUSTIFICACIÓN

A nivel mundial la nanotecnología y la nanociencia han abierto posibilidades en la innovación científica y tecnológica, además han tenido influencia en el ahorro de materiales y la reducción de contaminantes. Esta nueva revolución ha sido bien aceptada en industrias como la farmacéutica, textil o petroquímica, solo por citar algunos. Sin embargo, también existen avances en la agricultura y la gestión ambiental, pero estos son poco difundidos y aplicados.

En México, la investigación en nanotecnología aplicada a la agricultura tiene algunas limitantes: a) los materiales de investigación tienen costos elevados; b) se desconoce el procedimiento de obtención de los insumos, c) no se cuenta con la instrumentación adecuada, d) faltan evidencias de estudios de toxicidad en campo, e) el marco regulatorio para uso y liberación de nanomateriales en campos agrícolas es nulo; entre otros. Sin embargo, el abanico de posibles aplicaciones de avances nanotecnológicos en la agricultura es muy amplio: fertilizantes, detección de patógenos, biosensores, tratamiento de agua, recuperación de suelos, manejo pos-cosecha, entre otras aplicaciones.

El interés de empresas y del Estado en la nanotecnología agrícola está limitado por la incertidumbre ante los efectos aún desconocidos, toda vez que se trata de la producción de alimentos, una vía rápida para consumir nanomateriales. La presente investigación pretende presentar un panorama real de la nanotecnología aplicada a la agricultura, mostrándola como una herramienta útil en la búsqueda de la sustentabilidad, si las evidencias así lo permiten. Los nanomateriales podrían incrementar significativamente los rendimientos y la calidad de los alimentos, ligados a otros beneficios en materia de retorno de inversión, pero, las consideraciones ambientales, sociales y económicas también deberán ser tomadas en cuenta.

En los últimos años la nanotecnología ha favorecido el desarrollo de otras áreas científicas y tecnológicas, debido a la generación constante de nuevos materiales con propiedades particulares y con un sin número de aplicaciones. Lo anterior es evidente por el número de patentes que han sido registradas y por la publicación de miles de artículos científicos con enfoques nanotecnológicos en revistas de prácticamente todas las áreas del conocimiento. Sin embargo, ese interés por crear nuevos materiales o dispositivos de dimensiones nanométricas, también provoca incertidumbre y preocupación por los riesgos potenciales sobre la salud y el medio ambiente durante la síntesis, uso, liberación o disposición final. Así mismo, la inclusión de productos de dimensiones nanométricas en el mercado de agroquímicos e insumos agrícolas es una realidad que genera incertidumbre y preocupación sobre el potencial daño al medio ambiente y a la salud pública, aún a pesar de que algunos nanomateriales incrementan significativamente el crecimiento y desarrollo de los cultivos, así como sus componentes de rendimiento. Por lo anterior, es necesario documentar y evaluar las aplicaciones nanotecnológicas que se están comercializando en el sector agrícola mexicano, a fin de contribuir con el avance tecnológico al desarrollo sustentable.

6. HIPOTESIS

Las NP's de TiO_2 afectan las comunidades microbianas de la rizosfera de frijol común y sus componentes de rendimiento en los sistemas de producción agrícola debido a sus efectos fitotóxicos.

7. OBJETIVO GENERAL

Determinar el efecto de nanopartículas de TiO_2 sobre las plantas de frijol común (*Phaseolus vulgaris L.*) y las comunidades microbianas de la rizosfera de frijol común, cultivado en condiciones de invernadero.

8. OBJETIVOS PARTICULARES

- Cultivar frijol común en un suelo agrícola acondicionado con nanopartículas de TiO_2, bajo condiciones de invernadero.
- Caracterizar el crecimiento y desarrollo del cultivo con base en sus etapas

fenológicas.

- Evaluar las interacciones simbióticas frijol-rizobias y los componentes de rendimiento del cultivo.
- Extraer ADN de suelo de la rizósfera de frijol y analizar la diversidad y abundancia de sus comunidades microbianas.
- Identificar y analizar las investigaciones publicadas en revistas del Journal Citation Reports (JCR) del Web of Science™, relacionadas con el uso de nanopartículas en la producción de frijol y otros cultivos agrícolas.

IX. MATERIALES Y METODOS

La investigación consistió en dos etapas que a continuación se describen:

Etapa 1. Investigación experimental.

En esta parte se empleó metodología cuantitativa, mediante el establecimiento de un cultivo de frijol en condiciones de invernadero que fue acondicionado con nanopartículas de dióxido de titanio. Se midió la respuesta de la planta durante su ciclo de vida 90 días, así como el comportamiento de las poblaciones de microorganismos del suelo rizosférico por la aplicación de las nanopartículas. De modo que pudieran obtenerse datos sobre la interacción planta-nanopartículas-suelo (microorganismos). Se hicieron igualmente mediciones a la planta: Actividad fotosintética, crecimiento y desarrollo de estructuras (raíz, tallos y hojas) y rendimientos de cultivo. Se monitorearon las poblaciones microbianas mediante la extracción de ADN en suelo rizosferico mediante secuenciación con illumina. Al suelo se le midieron los contenidos de NO_3, NO_2, y amoniaco, así como otros parámetros fisicoquímicos.

Etapa 2. Búsqueda del Estado del Arte

En esta etapa se hicieron búsquedas de documentos específicos como:

Artículos científicos relacionados con la aplicación de nanopartículas de dióxido de titanio y otras NPS que estén relacionadas con la producción agrícola, cuyos contenidos estén enfocados en estudios ambientales, sociales, políticos, y biotecnológicos; informes estadísticos de instituciones gubernamentales, relacionados con nano materiales y producción agrícola, reglamentación vigente o en desarrollo en otros países sobre nanotecnologías para su aplicación en agricultura.

Esta tesis, está integrada por documentos que se han elaborado durante el desarrollo del proyecto, y se han publicado, o están en proceso de publicación. Dado la naturaleza transdiciplinar de la investigación, en cada documento se detalla la metodología seguida en cada uno de ellos, esto con el objetivo de evitar ser reiterativo en esta tesis.

X. **RESULTADOS Y DISCUSIÓN**

Los resultados y discusión se encuentran en los respectivos apartados de cada artículo o capítulo de libro.

10.1 ETAPA EXPERIMENTAL

10.1.1 Artículo 1. Growth and development of common bean (*Phaseolus vulgaris* l.) Var. Pinto Saltillo exposed to iron, titanium, and zinc oxide nanoparticles in an agricultural soil

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GROWTH AND DEVELOPMENT OF COMMON BEAN (*PHASEOLUS VULGARIS* L.) VAR. PINTO SALTILLO EXPOSED TO IRON, TITANIUM, AND ZINC OXIDE NANOPARTICLES IN AN AGRICULTURAL SOIL

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Abstract. Sustainable use of nanoparticles (NP) in the agriculture requires a deep understanding in order to determine their benefits potential as well as their toxicological impacts. Common bean plants were growing and irrigated with suspensions of magnetite, ferrihydrite, hematite, zinc oxide, or titanium dioxide NP at 0, 3, or 6 g L^{-1} in a 120 days' greenhouse experiment, in order to investigate the effect of these NP on growth and development of common bean. None of the five NP modified significantly the chlorophyll content of common bean plants, while at least one concentration of hematite, ferrihydrite or magnetite increased significantly the total N of roots or shoots, the number of pods, dry weight of pods, the number of seeds, and yield of common bean. Additionally, at least one concentration of zinc oxide or titanium dioxide decreased significantly the number of pods, the fresh weight of pods and the number of seeds. These finds are an important factor to take into account with regard to the applicability of NP for long-term use in crops, but the selection of the proper NP at their adequate concentration is important for realizing higher benefits for an agrosustainable target.
Keywords: *agro-food industry, agronanotechnology, chlorophyll content, potential hazard or risk of nanoparticles, sustainable development, nanofertilizer, Phaseolus vulgaris L.*

Introduction

While nanoparticles (NP) occur naturally in the environment and have been intentionally used for centuries, the production and use of engineered NP has seen a recent spike, which makes environmental release almost certain (Maurer-Jones et al., 2013). Keller et al. (2013) estimated that 63–91% of over 260,000–309,000 metric tons of global engineered nanomaterials production in 2010 ended up in landfills, with the balance released into soils (8–28%), water bodies (0.4–7%), and atmosphere (0.1–1.5%). It is well known that hundreds of NP are being used worldwide in a wide range

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of products or devices, however, at our knowledge there are not standardized techniques nor laws governing the proper management of NP during their production, distribution, use, and confinement. This implies that NP may be released into the environment despite their potential harmful effects on human and environmental health.

Among some properties that comprise the bean are their high content of iron, vital for a proper brain development, help to correct biliary disorders, rheumatic diseases, lower cholesterol level and is effective against anemia, and their consumption can prevent some types of cancer. Per 100 common bean grams, 20 g are protein, 5.8 g are fat and 3 g are fiber (Lépiz et al., 2010).

In some prior research conducted on this topic, the results were varied, some of them showed favorable aspects due to the use of nanoparticles as the case of Ma et al. (2010), whose experimental data evinced that the TiO_2 nanoparticles at concentrations of 2.5-40 g kg^{-1} soil, improved the growth of the spinach. Other results exhibited no significant effects, as presented by Doshi et al. (2008), where aluminum nanoparticles did not show a significant effect on common bean studies performed in sand columns with concentrations up to 17 mg L^{-1} of aluminum. In addition, some studies present negative effects on the development and growth of established crops. Canas et al. (2008) indicated that monolayer carbon nanotubes caused significant affectations in the root elongation of crops such as tomato, cabbage, carrot and lettuce.

There have been published some studies that intend to demonstrate that some metallic NP are able to increase the growth and development of some crops, i.e., the NP are used as if they were fertilizers (Burke et al., 2015; Rico et al., 2011). However, the potential effect of NP on yield and yield components has not been studied when NP are considered as a collateral consequence of the NP polluted environment. It is still a challenge assessing most of the effect of NP in natural soils. It should be noted that NP have different pathways, effects, fates and behaviors that might vary within living organisms, soils and contaminants (Cornelis et al., 2014; Rodrigues et al., 2016). In this regard, the objective of this research was to investigate the effect of different nanoparticles such as iron, titanium and zinc oxide on growth and development of common bean plants cropped in an agricultural soil under greenhouse conditions, as a contribution to the new emerging field called econanotoxicology.

Materials and methods

Experimental site

This study was carried out in a greenhouse of the 'Programa de Sustentabilidad de los Recursos Naturales y Energía del Cinvestav-Saltillo' located in Saltillo, Coahuila, Mexico. This area is located in the southeastern state of Coahuila, centered at 25° 31' N, 101° 37' W, at an altitude of 1,600 m above sea level. According to FAO/UNESCO soil classification system, the soil is a Haplic Xerosol with pH 7.3 and electrolytic conductivity 4.8 dS m^{-1}, a water holding capacity (WHC) of 865 g kg^{-1}, an organic carbon content of 1.5 g C kg^{-1} soil, and a total N content of 0.7 g N kg^{-1} soil.

Biological material

Common bean seeds were donated by 'INIFAP-Celaya, Mexico'. All seeds were kept in the dark at 4 °C until use. Pinto Saltillo was developed to solve the problem of

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traditional varieties of 'pinto' type, which has a reduced postharvest life, due to the accelerated darkening of the seed coat.

Nanomaterials

Nanoparticles of magnetite, ferrihydrite and hematite were manufactured according to Pariona (2012), while nanoparticles of zinc oxide and titanium dioxide were purchased from 'Materiales nanoestructurados S.A de C.V. (San Luis Potosí, México)'. Its crystallographic system was cubic, hexagonal or tetragonal (*Table 1*). The X-ray diffraction was conducted to verify the pure phase samples (*Fig. 1*), and the magnetic properties of the samples were measured by MicroMagTM 2900 Alternating Gradient Magnetometer (*Fig. 2*).

Table 1. *Physicochemical characteristics of nanoparticles used to irrigate common bean crop (Phaseolus vulgaris* L.*) in a 120 days greenhouse experiment.*

Oxide	Molecular formula	Color	Particle size	Crystallographic system	Magnetic properties
Magnetite	Fe_3O_4	Black	6 a 20 nm	Cubic	Superparamagnetic
Ferrihydrite	$FeOOH{\bullet}xH_2O$	Dark brown	2 a 3 nm	Hexagonal	Antiferromagnetic
Hematite	α-Fe_2O_3	Red ochre	80 a 94 nm	Hexagonal	Weakly antiferromagnetic
Zinc oxide	ZnO	White	< 50 nm	Tetragonal	Weakly ferromagnetic
Titanium dioxide	TiO_2	White	< 50 nm	Hexagonal	Weakly ferromagnetic

Cultivation of plants in the greenhouse

The full experimental setup was repeated three times. The first one was carried out from January to May, 2016, the second one, from February to June, 2016, and the third one from March to July, 2016. Sixty sub-samples of 3,500 g soil, i.e., five kinds of nanoparticles (nano-Fe_3O_4, nano-$FeOOH{\bullet}xH_2O$, nano-α-Fe_2O_3, nano-ZnO, and nano-TiO_2) × three replicates × four concentrations, were added to square plastic pots whose length, width, and height were 17 × 15 × 17 cm, respectively. Five treatments (nanoparticles) at four concentrations (zero, one, three, and six g L^{-1}) were applied to the soil during irrigation so that we sprayed each plastic pot with 500 mL of a zero, one, three, or six g nano L^{-1} suspension, throughout the experiment. Three seeds of common bean were planted in one hundred and eighty plastic pots, i.e., five nanoparticles × three replicates × four concentrations on three experiments. The seeds were placed at two cm depth in each plastic pot. Five days after planting, the seedlings were thinned to one plant per plastic pot. The plastic pots were placed in the greenhouse for 120 days. A plastic container was placed under each plastic pot to collect drained liquid. However, irrigation was well controlled so that no leaching was observed. Thirty, 60 and 120 days after sowing, three plastic pots were selected at random from each treatment and each concentration. The entire soil column was removed from the plastic pot and the 0-7.5 cm and 7.5-15 cm depth, where the samples were taken with care not to damage the root structure. The roots were manually separated from the shoots of the plant. Then the soil was carefully disaggregated with the hands to avoid the rupture of the roots. Subsequently, the soil was sifted gently to extract the pieces of root that may have been left in it, in order to be sure that 100% of the roots were removed, washed and weighed. After that, the root was extended and measured along with the shoots length. The roots

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and shoots were dried at 70 °C, were weighed and analyzed for Ti, Fe, Zn, and total N. The soils from 0-7.5 cm and 7.5-15 cm of depth were analyzed for pH, CE, Ti, Fe, and Zn. The amount of chlorophyll was quantified every two days after sowing, beginning at day 15 (*Fig. 3*). The temperature and moisture content inside the greenhouse during the experiment were 24 °C and 35-45%, respectively.

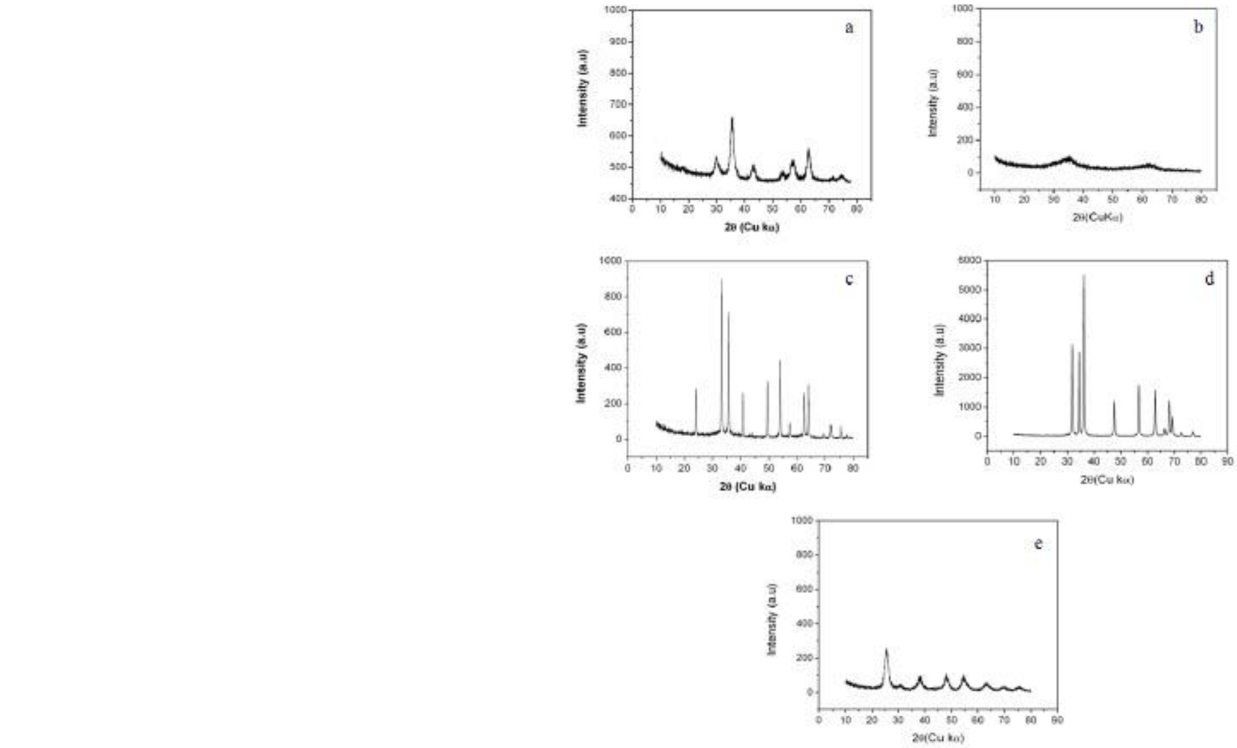

***Figure 1.** X-ray diffraction patterns of nanoparticles of a) Magnetite, b) Ferrihydrite, c) Hematite, d) ZnO, and e) TiO_2.*

Chemical analyses

The pH was measured in 1:2.5 soil or wastewater sludge/H_2O suspension using a 716 DMS Titrino pH meter (Metrohm Ltd. CH.-901, Herisau, Switzerland) fitted with a glass electrode (Thomas, 1996). The EC was determined in a 1:5 soil/H_2O suspension as described by Rhoades et al. (1989). The organic C in soil was measured in a total organic carbon analyzer TOC-VCSN (SHIMADZU, USA). The inorganic C was determined by adding 5 mL 1 M hydrogen chloride (HCl) solution to 1 g air-dried soil and trapping CO_2 evolved in 20 mL 1 M NaOH. Total N in soil, root and shoot was measured by the Kjeldahl method using concentrated H_2SO_4, K_2SO_4 and $CuSO_4$ to digest the sample (Bremner, 1996). Soil particle size distribution was defined by the hydrometer method as described by Gee and Bauder (1986). Water holding capacity

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was measured on 6.5 kg soil placed in a PVC tube (length 50 cm and ∅ 16 cm), water-saturated, stoppered with a PVC ring and left to stand overnight to drain freely. The WHC is defined as (Gardner, 1986), WHC = [(soil water-saturated - soil dried at 105 °C) / soil dried at 105 °C] * 1000. The units of WHC are expressed in g kg^{-1}. The amount of chlorophyll was measured with a Minolta SPAD-502 Chorophyll meter (Markwell et al., 1995). The Fe, Ti and Zn were determined by inductively coupled plasma mass spectrometry (ICP–MS).

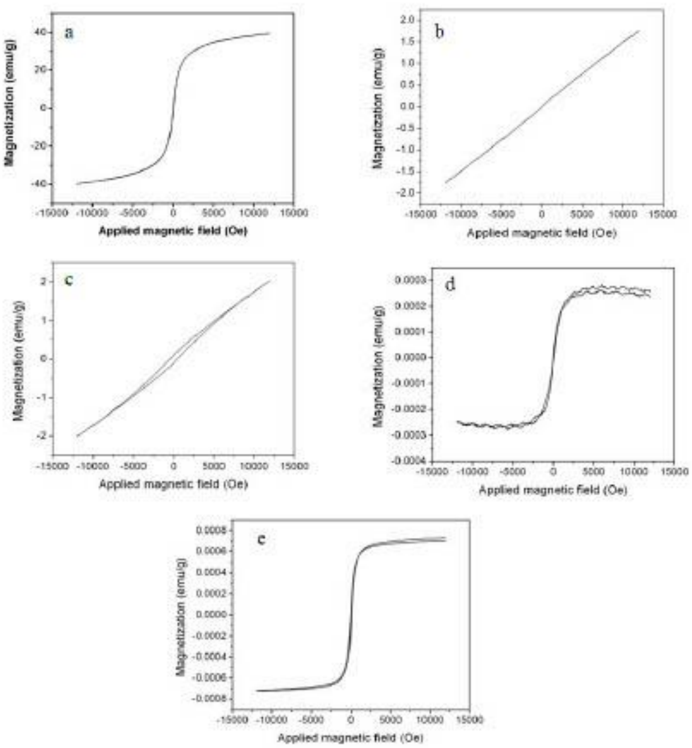

Figure 2. Magnetization curves of a) Magnetite, b) Ferrihydrite, c) Hematite, d) ZnO and e) TiO_2.

Statistical analyses

The data were subjected to an analysis of variance (ANOVA) and means compared with the Tukey test using Statistical Analysis System (SAS) software version 8.0 for Windows (SAS Institute, 1989). Soil and plant characteristics were subjected to one-way analysis of variance using a general lineal models procedure (PROC GLM) to test for significant differences between treatments ($P < 0.05$). Methodology for PCA analysis may be found in Fernández-Luqueño et al. (2016). All analyses were performed using the SAS statistical package (SAS Institute, 1989). All data presented

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were the mean of three replicates in soil from three different plots, while the whole experiment was repeated three times (n = 27), sampled after 30, 60, and 120 days.

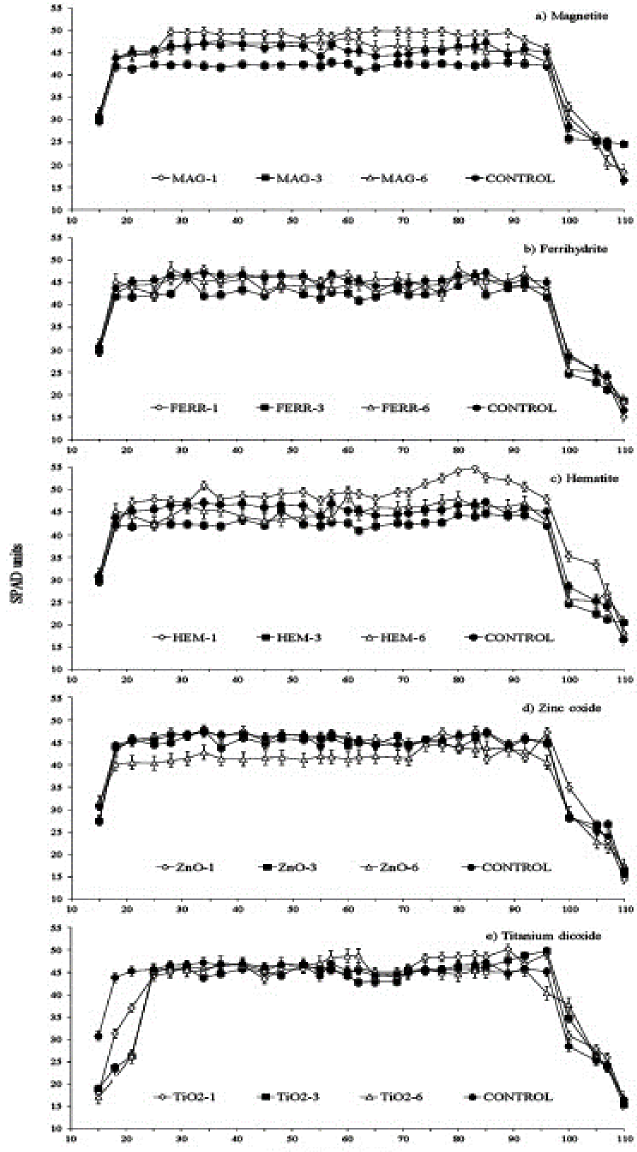

Figure 3. *SPAD units of bean plants (Phaseolus vulgaris L.) cultivated in an agricultural soil irrigated with 500 mL of zero, one, three, or six g nanoparticle L^{-1} suspension. Nanoparticles of Fe_3O_4, $FeOOH \cdot xH_2O$, α-Fe_2O_3, ZnO, and TiO_2 were used. Data are the mean of three pots × three different soils × three experiments × three measurements by each plant, i.e., n = 81. Each experiment lasted 120 days.*

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Results

SPAD units

The concentration of the chlorophyll quantified on leaves of common bean plants cultivated in an agricultural soil irrigated with 500 mL of zero, one, three, or six g nanoparticle L^{-1} suspension, during 120 days after sowing is shown in *Figure 3*. SPAD Units data are related to the chlorophyll content, which maintained slightly unchanged over the time with values between 40 to 50 SPAD units in most of the experiment, excepting the HEMATITE treatment (HEM-1) which the SPAD units reached 55. The lowers chlorophyll values were presented in all the treatments during the onset of the measurements and at the end of the growing stage, i.e., at 15 and 95 days after sowing, respectively.

Plant characteristics and crop yield

Most of the plant and yield characteristics (root fresh weight, root dry weight, root length, shoot fresh weight, shoot dry weight, shoot length, and SPAD units) were not significantly different between nanoparticles treatments, compared with the CONTROL treatment ($P < 0.05$) (*Table 2*). FERRIHYDRITE treatments at 3 and 6 g L^{-1} and HEMATITE at 1 g L^{-1} increased significantly the concentration of total N in roots, compared with the CONTROL treatment. All FERRIHYDRITE treatments and HEMATITE at 3 and 6 g L^{-1} increased significantly the concentration of total N in shoots, compared with the CONTROL treatment (*Table 2*).

The MAGNETITE and FERRIHYDRITE treatments at 6 g L^{-1} increased significantly the number of pods, compared with the CONTROL treatment. However, the ZINC OXIDE and TITANIUM OXIDE treatments at 6 g L^{-1} decreased significantly the number of pods, compared with the CONTROL treatment (*Table 2*). The fresh weight of pods decreased significantly when plants were amended with MAGNENTITA or HEMATITE at 3 or 6 g L^{-1}, and when they were amended with FERRIHYDRITE or ZINC OXIDE at 6 g L^{-1}, compared with the CONTROL treatment (*Table 2*). The dry weight of pods decreased significantly when plants were amended with FERRYDRITE at 3 g L^{-1}, but MAGNETITE at 3 or 6 g L^{-1} increased significantly the dry weight of pods, compared with the CONTROL treatment (*Table 2*). MAGNETITE and FERRIHYDRITE increased significantly the number of seeds when plants were amended with 6 g L^{-1}, while HEMATITE increased it significantly when plants were amended with 3 or 6 g L^{-1}. However, plants amended with ZINC OXIDE or TITANIUM DIOXIDE decreased significantly the number of seeds, compared to the CONTROL treatment. MAGNETITE or HEMATITE at 3 or 6 g L^{-1} and FERRIHYDRITE at 6 g L^{-1} increased significantly the yield, while ZINC OXIDE or TITANIUM DIOXIDE decreased it significantly, compared with the CONTROL treatment (*Table 2*). Nanoparticles did not affect significantly the SPAD units.

The seed number was strongly significantly correlated with fresh or dry weight of roots, length of root or shoot, total nitrogen of shoot, and with number, fresh or dry weight of pods (*Table 3*). Seed yield was strongly significantly correlated with fresh weight of root, total nitrogen of root, dry weight of shoot, total nitrogen of shoot, with number, fresh or dry weight of pods, and with seed number. In addition, SPAD units was strongly significantly correlated with total nitrogen of shoot and with yield (*Table 3*).

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***Table 2.** Characteristics of common bean (Phaseolus vulgaris L.) cultivated in an agricultural soil irrigated with 500 mL at zero, one, three, or six g nanoparticle L^{-1} suspension. The whole experiment was repeated three times (the first time, from January to May, 2016; the second one, from February to June, 2016; and the third one, from March to July, 2016). Each whole experiment lasted 120 days. Root and shoot data are the mean of values measured after 30, 60 and 120 d, i.e., n = 81. The pods and seeds data are the mean of values measured after 120 d, i.e., n = 27. SPAD unit's data are the mean of three measures twice a week during 14 weeks, i.e., n = 1,988 (3 soils × 3 replicates × 3 measures per plant × 3 sampling dates × 2 measures per week × 14 weeks).*

Treatments / g NP L^{-1}	Root [Θ]				Shoot				Pods			Seeds		SPAD
	Fresh weight	Dry weight	Length	Total Nitrogen	Fresh weight	Dry weight	Length	Total Nitrogen	Number	Fresh weight	Dry weight	Number	Yield	Units
Control														
0	13.6 a[Σ]	1.1 a	28.1 ab	25.8 c	17.9 a	2.8 a	21.4 ab	27.3 e	14.6 cd	20.5 de	5.5 cd	49.6 cd	3.6 fg	35.8 ab
Magnetite (Fe_3O_4)														
1	10.0 a	1.0 a	24.9 ab	26.4 bc	15.6 a	1.7 a	22.0 ab	30.3 cde	15.7 bcd	20.9 cde	5.9 c	48.7 cde	3.9 defg	38.4 a
3	11.3 a	0.8 a	24.0 ab	28.9 abc	14.5 a	1.5 a	22.7 ab	29.8 cde	16.3 bc	22.5 bc	6.6 ab	49.0 cde	4.8 ab	35.8 ab
6	13.5 a	1.2 a	19.0 ab	30.4 abc	17.3 a	1.9 a	25.9 b	32.1 bcde	17.3 ab	26.0 a	7.1 a	64.3 a	4.7 bc	36.4 ab
Ferrihydrite ($FeOOH•xH_2O$)														
1	11.8 a	1.0 a	28.9 ab	30.5 abc	17.8 a	2.6 a	21.4 ab	33.8 abcd	14.7 cd	20.7 cde	5.5 cd	55.0 bc	3.6 g	36.0 ab
3	11.6 a	1.1 a	27.8 ab	32.1 a	16.7 a	2.9 a	21.9 ab	34.9 abc	15.3 bcd	20.3 cd	4.5 e	51.0 cd	3.8 efg	36.0 ab
6	12.3 a	1.3 a	27.1 ab	32.0 a	15.7 a	2.7 a	19.2 ab	35.0 abc	19.3 a	26.9 a	5.6 cd	67.0 a	4.2 cd	36.6 ab
Hematite (α-Fe_2O_3)														
1	14.7 a	1.3 a	25.1 a	31.0 ab	18.3 a	3.0 a	20.2 ab	32.3 bcde	15.7 bcd	22.0 bcd	5.5 cd	53.7 bcd	4.0 def	37.6 ab
3	14.3 a	1.3 a	28.2 ab	30.0 abc	19.5 a	3.2 a	17.0 ab	37.2 ab	15.0 cd	23.6 b	5.9 c	60.0 ab	5.2 a	35.7 ab
6	14.8 a	1.4 a	31.0 ab	30.0 abc	18.1 a	2.9 a	19.4 ab	38.5 a	16.0 bcd	25.9 a	5.9 bc	60.7 ab	5.1 a	36.6 ab
Zinc Oxide (ZnO)														
1	11.1 a	0.9 a	21.2 ab	28.1 abc	15.7 a	2.4 a	17.0 ab	29.8 cde	15.0 cd	19.4 e	5.2 cde	45.3 def	4.0 defg	35.3 ab
3	11.9 a	1.0 a	19.6 ab	29.1 abc	15.5 a	2.2 a	15.7 a	30.2 cde	15.3 bcd	21.1 cde	5.5 cd	40.7 ef	3.9 defg	34.9 ab
6	13.1 a	0.8 a	21.1 ab	28.6 abc	16.8 a	2.6 a	18.2 ab	30.4 cde	12.3 e	23.8 b	5.2 cde	37.7 fg	4.1 de	36.7 ab
Titanium dioxide (TiO_2)														
1	11.1 a	0.9 a	17.6 ab	27.7 abc	13.8 a	2.1 a	17.5 ab	28.3 e	14.0 de	19.2 e	5.0 de	31.3 gh	4.0 defg	34.7 b
3	11.9 a	1.0 a	17.1 b	30.0 abc	13.3 a	2.4 a	15.7 a	28.8 de	15.7 bcd	21.1 de	5.3 cd	23.7 h	3.9 defg	35.7 ab
6	11.5 a	1.0 a	22.0 ab	28.5 abc	18.2 a	2.0 a	16.3 a	29.5 de	12.0 e	21.9 bcd	5.0 de	26.3 h	4.1 de	34.2 b
MSD[π]	9.05	0.64	13.5	5.0	9.4	1.7	9.2	5.4	2.0	1.9	0.7	8.5	0.4	3.5

[Θ]Fresh or dry weights are expressed in g; Length is in cm; Total nitrogen is in g N kg^{-1} dry plant; Yield is in g per plant.
[Σ]Values with the same letter within the columns are not significantly different ($P < 0.05$).
[π]Minimum significant difference ($P < 0.05$).

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***Table 3.** Correlations between characteristics of common bean crop (Phaseolus vulgaris L.) cultivated in an agricultural soil irrigated with 500 mL at zero, one, three, or six g NP L^{-1} suspension. Data were pooled among five treatments, three soils and the three replicates of the whole experiment. Each experiment lasted 120 days.*

Plant characteristics	Root[ø]				Shoot				Pods			Seeds	
	Fresh weight	Dry weight	Length	Total Nitrogen	Fresh weight	Dry weight	Length	Total Nitrogen	Number	Fresh weight	Dry weight	Number	Yield
Root dry weight	0.867***												
Root length	0.891***	0.834***											
Root total N	-0.238***	0.005	-0.289***										
Shoot fresh weight	0.839***	0.870***	0.762***	0.142									
Shoot dry weight	0.894***	0.876***	0.852***	-0.062	0.883***								
Shoot length	0.848***	0.815***	0.809***	-0.075	0.837***	0.780***							
Shoot Total N	-0.037	0.245***	-0.041	0.839***	0.313***	0.150	0.121						
Pods number	0.279	0.428***	0.210	0.155	-0.064	-0.108	0.297***	0.166					
Pods fresh weight	0.344***	0.462***	0.155	0.332***	-0.278	-0.121	0.078	0.501***	0.292***				
Pods dry weight	0.062	0.130***	0.023	0.005	-0.218	-0.429***	0.379***	0.112	0.272	0.341***			
Seed number	0.415***	0.616***	0.647***	0.058	0.115	0.195	0.492***	0.421***	0.480***	0.400***	0.343***		
Seed yield	0.200***	0.241	0.060	0.396***	-0.183	-0.301***	-0.013	0.622***	0.276**	0.475***	0.295***	0.270***	
SPAD Units	-0.039	0.001	-0.008	0.099	-0.014	-0.017	0.023	0.186***	0.182	0.122*	0.121	0.149	0.341***

*P < 0.005; **P < 0.001; ***P < 0.0001

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Principal component analysis

Loading for parameters obtained after VARIMAX rotation are given in *Table 4*. The plants characteristics had three significant PCs. The first principal component (PC1) explained 31% of variation and was related to root fresh weight, root dry weight, root length, shoot total nitrogen, number of pods, pod fresh weight, seed yield, number of seeds, and SPAD units. The second principal component (PC2) explained 20% of variation and was related to shoot fresh weight and shoot dry weight, while the third principal component (PC3) explained 14% of variation and was related to root total nitrogen but negatively related to shoot length and pod dry weight. The three principal components explained 65% of variation (*Table 4*).

On the scatter plot with PC1 and PC2, the kinds of NP or their concentrations are clearly separated from each other (*Fig. 4a*). HEMATITE and FERRIHYDRITE can be found in the upper right quadrant, while MAGNETITE, ZINC OXIDE or TITANIUM DIOXIDE lie in the two left quadrants. The CONTROL treatment lies in the lower left quadrant (*Fig. 4a*). On the scatter plot with PC1 and PC3, the treatments are visually distinct (*Fig. 4b*). The HEMATITE, FERRIHYDRITE, and CONTROL treatments lie in the two-right quadrant, while MAGNETITE, ZINC OXIDE or TITANIUM DIOXIDE lie in the two left quadrants (*Fig. 4b*).

Table 4. *Rotated loading on the PC of bean plants characteristics (Phaseolus vulgaris L.) cultivated in an agricultural soil irrigated with 500 mL at zero, one, three, or six g NP L^{-1} suspension. NP of Fe_3O_4, $FeOOH{\cdot}xH_2O$, α-Fe_2O_3, ZnO, and TiO_2 were used. Data were pooled among the five treatments and three experiment repetitions. The whole experiment was repeated three times (from January to May 2015; the second one from February to June 2015; and the third one from March to July 2015). Each whole experiment lasted 120 days.*

Statistical and measurements	Principal components [a]		
	PC1	PC2	PC3
Eigenvalues	4.27	2.83	1.94
Proportions	0.31	0.20	0.14
	Rotated loading on three retained components		
Root fresh weight	65*[,b]	14	30
Root dry weight	80*	32	5
Root length	67*	61	-9
Shoot fresh weight	20	74*	10
Shoot dry weight	24	79*	42
Shoot length	35	12	-80*
Root total nitrogen	33	-50	59*
Shoot total nitrogen	70*	-31	44
Number of pods	57*	-10	-26
Pod fresh weight	64*	-40	6
Pod dry weight	36	-37	-54*
Seed yield	52*	-60	12
Number of seeds	80*	17	-29
SPAD units	43*	-31	-9

[a]Only principal components with Eigenvalues>1 and that explain > 10% the total variance were retained
[b]Parameters with significant loading (> 0.4) on the within column principal component.

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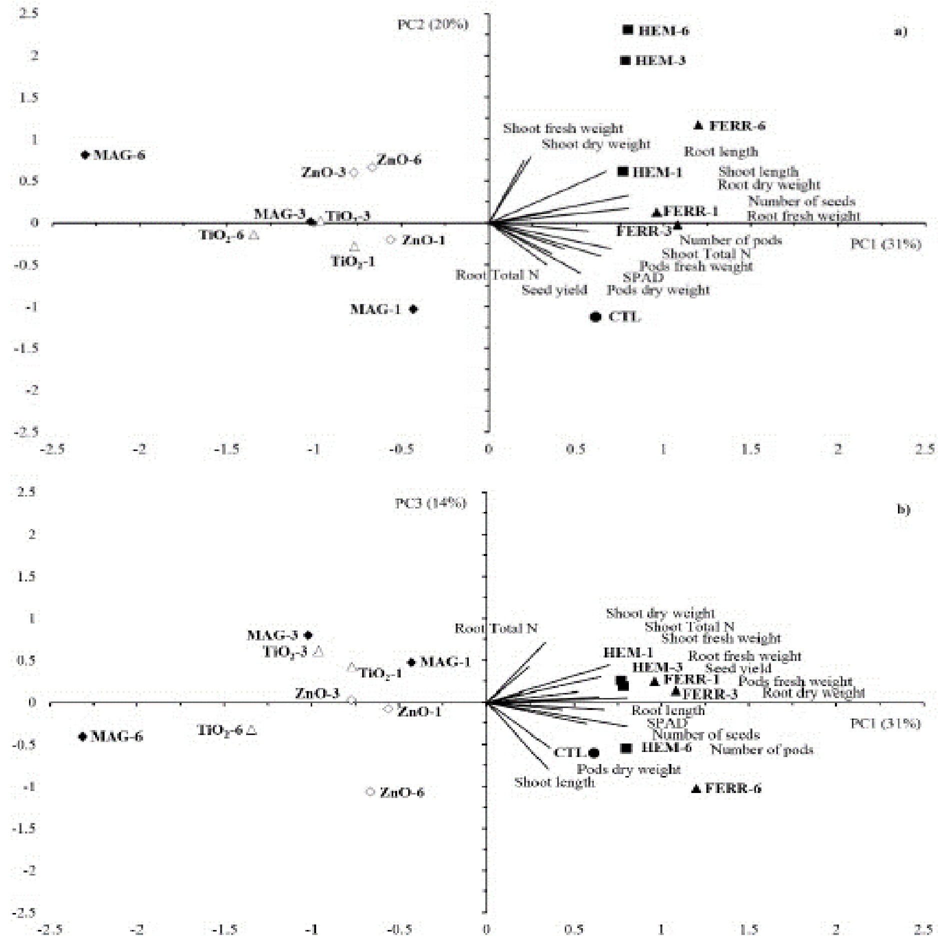

Figure 4. Principal component analysis performed on characteristics of bean plants (Phaseolus vulgaris L.*) cultivated in an agricultural soil irrigated with 500 mL of zero, one, three, or six g nanoparticle L^{-1} suspension. Nanoparticles of Fe_3O_4, $FeOOH{\cdot}xH_2O$, α-Fe_2O_3, ZnO, and TiO_2 were used. Data are the mean of three square plastic pots with 3.5 kg dry soil each one, for three different soils and three experiments, i.e., n = 27. Each whole experiment lasted 120 days. The first two factors explain 51% of the variation. MAG-1 (500 mL of 1 g NP-Fe_3O_4 suspension), MAG-3 (500 mL of 3 g NP-Fe_3O_4 suspension), MAG-6 (500 mL of 6 g NP-Fe_3O_4 suspension); FERR-1 (500 mL of 1 g NP-$FeOOH{\cdot}xH_2O$ suspension), FERR-3 (500 mL of 3 g NP-$FeOOH{\cdot}xH_2O$ suspension), FERR-6 (500 mL of 6 g NP-$FeOOH{\cdot}xH_2O$ suspension); HEM-1 (500 mL of 1 g NP-α-Fe_2O_3 suspension), HEM-3 (500 mL of 3 g NP-α-Fe_2O_3 suspension), HEM-6 (500 mL of 6 g NP-α-Fe_2O_3 suspension); ZnO-1 (500 mL of 1 g NP-ZnO suspension), ZnO-3 (500 mL of 3 g NP-ZnO suspension), ZnO-6 (500 mL of 6 g NP-ZnO suspension); TiO_2-1 (500 mL of 1 g NP-TiO_2 suspension), TiO_2-3 (500 mL of 3 g NP-TiO_2 suspension), and TiO_2-6 (500 mL of 6 g NP-TiO_2 suspension).*

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Discussion

All treatments showed a lower chlorophyll content during the onset of the measurement at 15 days after sowing. This behavior suggests that the common bean plants were not in the fullness of the photosynthetic process. SPADS curves commonly show a decreasing trend due to the measurement was done leaf by leaf at the beginning of vegetative growth (Ribeiro de Cunha et al., 2015). About the SPAD units, Gómez et al. (2011) reported values near to 40 – 45 SPAD units. Anderson and Ryser (2015). However, measured leaves chlorophyll concentration in common bean reported range between 30 and 40 SPAD units. In this study, none of the treatments increased the chlorophyll content of bean plants, nevertheless the SPAD units' values are consistent with the values reported by other authors. Fernández-Luqueño et al. (2008, 2010) stated that the SPAD units decreased abrupt and significantly as soon as onset the plant senescence processes. Additionally, Hong et al. (2005) reported that leaves of spinach (*Spinacia oleracea* L.) treated with TiO_2 nanoparticles had higher levels of photosynthesis compared to untreated leaves.

Several studies on the application of nanoparticles in a relatively broad range of species have attempted to understand the effect on plant growth. For instance, Lin and Xing (2007) reported that ZnO nanoparticles can inhibited seed germination of ryegrass. On the other hand, Stampoulis et al. (2009) did not found a cause-effect on seed germination, root elongation and biomass of zucchini (*Cucurbita pepo* L.) amended with nanoparticles in hydroponic solutions. In this study root fresh weight, root dry weight, root length, shoot fresh weight, shoot dry weight, shoot length, and SPAD units were not significantly different between nanoparticles treatments, compared to the CONTROL treatment ($P < 0.05$), i.e., NP did not change significantly some biomass parameters such as root or shoot dry weight. NP did not affect significantly the growing processes, but whether some characteristics related to yield components such as those linked to pods or seeds. It is assumed that in this study the NP-induced toxicity might not affect the plant growth. However, it has to be noted that other modes of actions as photo-induced toxicity and NP-dissolved ion effects might elicit toxicity (Fernández-Luqueño et al., 2014).

In this research, we found that at least one concentration of HEMATITE, FERRIHYDRITE or MAGNETITE increased significantly the total N of roots or shoots, the number of pods, dry weight of pods, the number of seeds, and yield of common bean. Burke et al. (2015) reported that Fe_3O_4 nanoparticles can affect the root system as wells as leaf phosphorous content from soybean plants (*Glycine max* (L.) Merr.), but Quoc et al. (2014) found that iron NP increased up 16% the yield of soybean in comparison with the control sample. In addition, Martinez-Fernandez et al. (2016) found reduction of the root functionality from sunflower plants (*Helianthus annuus* L.) by iron oxide nanoparticles. On the other hand, at least one concentration of HEMATITE, FERRIHYDRITE or MAGNETITE decreased significantly the fresh or dry weight of pods. Jeyasubramanian et al. (2016) stated that Fe_2O_3 nanoparticles increased the stem and root lengths and biomass production of spinach plant (*Spinacia oleracea* L.), while the effects were dependent of time and dose.

At least one concentration of ZINC OXIDE or TITANIUM DIOXIDE decreased significantly the number of pods, the fresh weight of pods and the number of seeds. Jacob et al. (2013) found that TiO_2 NP did not affect biomass production in common bean plants grown in nutrient solutions at 0, 6, and 18 mmol Ti L^{-1}. However, Adhikari et al. (2016) stated that application of nano-zinc oxide particles enhanced the auxin

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indole-3-acetic acid (IAA) production in plant roots of maize (*Zea mays* L.), soybean (*Glycine max* L.), pigeon pea (*Cajanas cajan* L.), and ladies finger (*Abelmoschus esculentus* L.), which subsequently improved the overall growth. In addition, it has been reported that independent of NP type, a concentration of 250 mg kg^{-1} of TiO_2 and ZnO NP promoted the highest plant height, root length, and biomass (Raliya et al., 2015). These authors stated that zinc oxide NP had a twin role of being an essential nutrient and a co-factor for nutrient mobilizing enzymes.

It is well known that NP are up taken by the vascular network but the accumulation rate in tissue is different for root and shoot systems from each plant species, while each NP type might have a differential interaction ship with cells as effect of the growing stage, NP size, time exposition, and biotic and abiotic factors. These considerations could be the main reason for the wide variability of results when attempting know the effects of NP on plants. Additionally, it has to be highlighted that some plants NP-treated do not show any observable phenotypic changes in overall growth indicating that environmental NP pollution could be dangerously unnoticed.

Conclusions

None of the five kinds of NP used in this experiment (magnetite, ferrihydrite, hematite, zinc oxide or titanium dioxide) modified significantly the chlorophyll content of common bean plants as witnessed by the SPAD units' values. However, nanoparticles of magnetite, ferrihydrite, hematite, zinc oxide or titanium dioxide modified significantly at least one plant characteristic or one yield component of common bean, such as SPAD units, root length, root total N, shoot length, shoot total nitrogen, pod number, pod fresh weight, pod dry weight, seed number or yield. The nanoparticles with Fe such as magnetite, ferrihydrite, or hematite were those that increased significantly more crops characteristics such as total N of roots or shoots, the number of pods, dry weight of pods, the number of seeds, and yield of common bean. These finds are an important factor to take into account with regard to the applicability of NP for long-term use in crops but, the selection of the proper NP at their adequate concentration is important for realizing higher benefits for an agrosustainable target. Additionally, there is the need of generating more data on chronic effects from long terms and concentration exposure of nanoparticles in plants, which is important for a better understanding of the potential hazard or risk of these nanoparticles, while more studies are also necessaries in order to identify the highest potential of NP in the rural sector and in the agro-food industry worldwide.

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10.1.2 Artículo 2. Rizospheric bacterial communities of common bean plants (*Phaseolus vulgaris* l.) Grown in an agricultural soil contaminated with TiO_2 nanoparticles. (En preparación)

En preparación. Será publicado en 2020 en la Revista: PLANT AND SOIL

Rhizospheric bacterial communities of common bean plants (*Phaseolus vulgaris* L.) grown in an agricultural soil contaminated with TiO_2 nanoparticles

Abstract

Background and aims The use of nanoparticles has increased substantially over the years and most of them will end up most likely in soil where their effect on the plant biome and the soil microbial community is still largely unknown.

Methods Bean plants (*Phaseolus vulgaris* L.) were cultivated in soil amended with 0, 150 or 300 mg TiO_2 nanoparticles kg^{-1} while plant development and its biome, nodule formation and the soil and rhizospheric microbial community were monitored.

Results

Conclusion

Keywords

Abundance and diversity of soil microorganisms, agricultural nanotechnology, crop production, healthy soil, soil pollution.

Introduction

Nanotechnology is a fast-growing research field with many applications in medicine, energy production, agriculture, electronics, drug administration and medical diagnostics

(Nowack and Bucheli 2007; Hu et al. 2010; Roco et al. 2011). The production of engineered nano-sized particles, i.e. < 100 *n*m, has reached 260,000-309,000×10^3 kg in 2010 (Keller et al. 2013). Large amounts of these nanoparticles (≤ 28%) could end up in the soil, water (≤7%) and in the atmosphere (1.5%) (Keller et al. 2013). TiO_2 nanoparticles (nTiO_2) are one of the most used nanomaterials. It is turbid with a whitish appearance and its photocatalytic activity has been used in products, such as paints, colorants, plastics, cosmetics, cleaning and personal care products, toothpaste and sunscreen (Jacobs et al. 2010). In the Unites States, the production of nTiO_2 could reach 2.5 million tons by 2025 and large amount could end up in the environment (Robichaud et al. 2009).

nTiO_2 could affect plants and soil organisms. Plants naturally interact with titanium as it is the second most abundant transition metal in soil, i.e. on average 6.3 mg/kg (Feizi et al. 2012). Titanium can change the content of some essential element in plant tissues and infer in the activity of some enzymes (peroxidase, catalase, and nitrate reductase) (Hrubý et al. 2002). Engineered nTiO_2 could have a negative or positive effect on plant growth (Feizi et al. 2012). There is no consensus on how plants respond to nTiO_2, but the reactivity of nanoparticles (NPs) depends on their composition, form, weight, size, aggregation, sedimentation or diffusion into the cell, soil conditions, dose and method of application and plant conditions (Lin et al. 2008; Lee et al. 2008, Sunada et al. 2008; Seeger et al. 2009; Raliya et al. 2016). At certain concentrations Fe_3O_4, ZnO, TiO_2, Ag and SiO_2 NPs improve plant development, such as germination, antioxidant and enzymatic activity, synthesis of chlorophyll and growth (Lu et al. 2002; Bao-shan et al. 2004; Zheng et al. 2005; Gao et al. 2008; Pandey et al. 2010; Wang et al. 2011; Feizi et al. 2012; Suriyaprabha et al. 2012; Wang et al. 2013). Bao-shan et al. (2004) applied nano-SiO_2

($nSiO_2$) to *Larix olgensis* H. var. changpaiensis seedlings and found that $nSiO_2$ improved root length, mean height, root collar diameter and number of lateral roots. $nTiO_2$ did not affect root elongation of oilseed rape (*Brassica napus* L.), wheat (*Triticum aestivum* L.), arabidopsis (*Arabidopsis thaliana* L.), cucumber (*Cucumis sativus* L.), lettuce (*Lactuca sativa* L.), rice (*Oryza sativa* L), and radish (*Raphanus sativus* L.) (Boonyanitipong et al. 2011; Larue et al. 2011; Wu et al. 2012). Asli and Neumann (2009) found that $nTiO_2$ inhibited leaf growth and transpiration as the root water transport was inhibited in maize seedlings.

It is important to understand a possible effect of nanoparticles on the plant roots. Priester et al. (2012) observed that CeO_2 nanoparticles affected the growth and nitrogen fixation in soybean nodules. Dimkpa et al. (2015) applied nanoparticles of ZnO (nZnO) to *Phaseolus vulgaris* L. and they reported a reduction of root ferric reductase activity with 31% suggesting a nano-specific contribution of the nZnO. They reported no significant changes in the population of *Pseudomonas chlororaphis* O6. Fan et al. (2014) found that the exposure of garden peas (*Pisum sativum* L.) to $nTiO_2$ decreased the number of secondary lateral roots. They also probed cultured *R. leguminosarum* Viciae 3841 as its common rhizobial partner of the plant and found alterations in the morphology of cultivated bacterial cells. The interaction between plant and bacteria was also affected by $nTiO_2$. Root nodule development and N_2 fixation were reduced. The polysaccharide composition of the walls of the nodules was also altered. This infers that the exposure to $nTiO_2$ could induce a response in host plants.

The accumulation of certain nanoparticles (NP) alters the activity, diversity, abundance and growth of soil microorganisms (León-Silva et al. 2016; Zhai et al. 2016; Samarajeewa et al. 2017). Ge et al. (2011) reported that $nTiO_2$ changed the abundance and diversity of bacterial communities in grassland soil and that the relative abundance of bacteria involved in refractory organic compound mineralization increased and those potentially involved in methane oxidation and N_2 fixation decreased. Beans have a symbiotic relationship with N_2 fixing bacteria, but it is unknown if $nTiO_2$ would affect this and thus the development of the plants. The aim of this work was to study the effect of $nTiO_2$ on i) bean plant development, ii) the bacterial community in soil cultivated with common bean plants (*Phaseolus vulgaris* L.), and iii) the bacterial communities in the rhizosphere and iv) bean plants.

Materials and methods

Common bean, soil and nanoparticles

Common bean (*Phaseolus vulgaris* L.) var. Pinto Saltillo certified seeds were purchased from *"El Instituto Nacional de Investigaciones Forestales, Agrícolas y Pecuarias"* (INIFAP-Celaya, México'). The seeds were stored in the dark at 4 °C until used.

Uncoated $nTiO_2$ were purchased from 'Materiales Nanoestructurados S.A de C.V. (San Luis Potosí, México). Physicochemical characteristics of $nTiO_2$ where provided by the manufacturer and are given in Table S1.

Soil was sampled at the Institute of Agricultural Sciences of the Autonomous University of Hidalgo State (Hidalgo State, Mexico) latitude north 20°04'53", latitude west 98°22'07". Soil was collected from three 2000 m^2 areas. The 0-20 cm top soil layer was sampled, passed through a 2 mm sieve and characterized.

The agricultural soil was a haplic *phaeozem* (FAO/UNESCO soil classification system) with pH 7.54 and electrolytic conductivity (EC) 5.3 dS m^{-1}, a water holding capacity (WHC) of 625 g kg^{-1}, an organic carbon content of 3.6 g C kg^{-1} dry soil, and a total N content of 0.21 g N kg-1 dry soil.

Experimental design and greenhouse experiment

Six different treatments were applied to the arable soil combining the application of 0, 150 and 300 mg nTiO2 kg-1 dry soil and soil left un cultivated or cultivated with common bean (*Phaseolus vulgaris* L.*)*. Plant development, plant bacterial biome and the bacterial community in the non-rhizospheric and rhizospheric soil was determined at day 0, 45 and 90. The experiment was done in a greenhouse at Cinvestav-Zacatenco. A completely randomized block design was used.

One hundred sixty two PVC columns (17 cm in diameter × 60 cm in height) closed on the bottom with perforated PVC lid and containing tezontle or porous, highly oxidized, volcanic rock (0.5 kg) on the bottom were filled with 7 kg soil. Three bean seeds were planted at 2 cm of deep. Titanium dioxide NPs were suspended in 200 ml deionized water and sonicated for 30 min. Each soil column was amended with 0, 150 or 300 mg $nTiO_2$ kg^{-1} dry soil at the time of sowing. The PVC columns were placed in the greenhouse for 90 days. One week after emergence, seedlings were thinned and only one (the most vigorous) plantlet was kept per column. Three PVC columns were selected at random from each treatment (n = 6) after 45 and 90 days. Plants were by shaken by hand for 5 min and the detached soil discarded. The rhizosphere was considered as the soil firmly adhered to the roots. Soil was brushed from the roots, while the bulk soil was taken from the 0-20 cm soil layer 10 cm from the bean plants. The soil was characterized and extracted for DNA as described below. The root and shoot length and fresh weight were determined. The roots and shoots were dried at 70 °C and weighed.

Plant chlorophyll content was determined on four aleatory leaves from three plants of each treatment using a Minolta SPAD-502 chlorophyll meter (Markwell et al. 1995) every two days starting 12 days after sowing. Plants were irrigated every third day during 90 days. Irrigation during plant growth was controlled so that no leaching occurred. The temperature was on average 25°C and the moisture content inside the greenhouse between 35-48%.

Soil and nanoparticles characterization

The gravimetric soil moisture content was determined by drying soils at 120°C for 48 hours and the WHC of the soil were determined as described earlier (Gardner, 1986) (. The EC (Rhoades et al. 1989) was determined in a 1:5 soil/H_2O suspension in water paste with a HI 933300 microprocessor (HANNA Instruments, USA). The pH was determined in a 1:2.5 soil/H_2O suspension soil-water paste using a calibrated potentiometer (Denver Instrument, USA) (Thomas 1996) with a glass electrode (3007281 pH/ATC Termofisher Scientific, USA). Soil particle size distribution was determined by the hydrometer method as described by Gee and Bauder (1986). A 10 g sub-sample of soil was extracted with 100 ml 0.5 M K_2SO_4 and the mineral N (NO_3-, NO_2- and NH_4^+) content in the extract was measured using a SKALAR Automatic Analyzer System (Mulvaney 1996).

A JEOL 2000 EX (JEOL Ltd. Tokyo, Japan) transmission electron microscope operated at 80 kV was used to evaluate the size and morphology of the NPs. The software ImageJ was used to measure the particles.

DNA extraction and PCR amplification

A 0.5 g sub-sample of soil was used for each extraction. The samples were washed with 0.15 mol L^{-1} of sodium pyrophosphate until the samples were clear. Excess pyrophosphate was removed with 0.15 mol L^{-1} of phosphate buffer pH 8 (Ceja-Navarro et al. 2010). The DNA was extracted using three different methods of cellular lysis and for each extraction a washed 0.5 g soil sub-sample was used (Hoffman and Winston 1987; Sambrook and Russell 2001; Valenzuela-Encinas et al. 2008). The metagenomic DNA obtained with the three techniques was pooled. The hypervariable regions V3 and V4 of the bacterial 16S rRNA gene were amplified by PCR. The PCRs products were pooled and purified using the QIAquick PCR purification kit (Qiagen, Germany) and quantified with a Nanodrop 3300 (TermoFisher, USA) with PicoGreen dsDNA. The samples were mixed in equimolar amounts and sequenced with an Ilumina MiSeq by Macrogen Inc. (Seoul, Korea).

Analysis of ILLUMINA secuencing data

The QIIME version 1.9.0 software pipeline was used to analyse the sequencing data (Caporaso et al. 2010). First, poor quality reads were excluded from further analysis, i.e. no ambiguous base calls and quality values less than 25 Phred Q score. Paired-end sequences were assembled with fastq-join method within QIIME. Operational taxonomic units (OTU) were clustered at 97% similarity level with UCLUST algorithm (Edgar 2010). Chimeras were detected and removed from the data using the Chimera Slayer (Haas et al. 2011).

Sequence alignments were done against the Greengenes core set and using representative sequences of each OTU using PyNAST, and filtered at a threshold of 75% (Caporaso et al. 2009). Taxonomic assignment was done by using the naïve Bayesian rRNA classifier from the Ribosomal Data Project (Wang et al. 2007) at a confidence threshold of 80%.

Phylogenetic and statistical analysis

All statistical analyses were done in R (R Core Team 2013). An ANOVA test (aov function) was used to determine the effect of NPs on plant development. A non-parametric test was used to determine the effect of the $nTiO_2$ application rate on the relative abundance of the different bacterial groups. The t1way test of the WRS2 package (A collection of robust statistical methods) was used (Mair and Wilcox 2017). Abundance of the different microbial taxonomic levels was explored separately with a principal component analysis (PCA) and the constrained analysis of principal coordinates (CAP) was used to explore the effect of treatment on the bacterial groups and soil characteristics. A PERMANOVA test was used to determine the effect of nanoparticles (0, 150 and 300 mg TiO_2 kg^{-1}), soil (bulk, non-rhizospheric and rhizosphere) and time (day 0, 45 and 90) and their interaction on the bacterial groups. The PCA, CAP and PERMANOVA tests were done with the vegan package (Oksanen et al. 2017). Heatmaps were constructed with the heatmap package (Kolde 2015). Sub-samples (n = 2) were averaged over the plots prior to the statistical analysis. A possible effect of the different soil characteristics (WHC, pH, water content, EC and mineral N (sum of NH_4^+, NO_2^- NO_3^-)), amount of nanoparticles (0, 150 or 300 mg $nTiO_2$ kg^{-1}), soil (bulk, non-rhizospheric or rhizosphere soil) and time (day 0, 45 or 90) on the relative abundance of the different microbial groups was explored with the random Forest package (Breiman and Cutler 2015).

Data accessibility

Sequence reads generated in this study were submitted to the NCBI Sequences Read Archive under accession number.

Results

Plant and soil characteristics

The SPAD units ranged between 25.8 and 50.9 SPAD (Fig. $$). Lower chlorophyll values were found at the onset of the experiment, i.e. 12 days after sowing and at the end. The application of $nTiO_2$ had no significant effect on the chlorophyll content of the plants and on the plant characteristics. In the table 3S are shown results of soil dynamic.

Bacterial community structure

The amount of TiO_2 applied to soil had no effect on the alpha diversity, except for the Chao1 index that was significantly higher in the rhizosphere soil applied with 300 mg TiO_2 kg^{-1} than in the unamended rhizosphere soil ($p = 0.017$) (Table 2). The alpha diveristy indexes were also similar in the bulk, non-rhizospheric and rhizosphere soil, except for the Chao1 index that was significantly higher in the rhizosphere soil applied with 300 mg TiO_2 kg^{-1} than in the bulk soil applied with 300 mg TiO_2 kg^{-1} (p = 0.024).

Table 2. Effect of nanoparticles (0 mg TiO2 kg^{-1} soil) and location (bulk, non-rhizospheric and rhizosphere soil) on the alpha diversity indexes.

	Chao1				
TiO_2 (mg kg^{-1})	Bulk soil	Non-rhizospheric soil	Rhizosphere	F value	P value
0	2154 a [a] A [b]	2119 a A	1666 b A	4.22	0.101
150	1704 a A	1599 a A	1822 ab A	0.15	0.866
300	1917 a B	1728 a B	2419 a A	7.52	0.024
F value	1.54	2.07	11.60		
P value	0.279	0.228	0.017		
	Shannon index				
0	8.96 a A	8.97 a A	7.48 a A	0.58	0.632
150	8.60 a A	8.89 a A	8.65 a A	0.63	0.574
300	9.03 a A	8.84 a A	9.22 a A	2.47	0.197
F value	0.36	1.54	1.72		
P value	0.713	0.328	0.352		
	Simpson				
0	0.994 a A	0.994 a A	0.935 a A	1.22	0.434
150	0.985 a A	0.994 a A	0.988 a A	2.34	0.199
300	0.995 a A	0.994 a A	0.995 a A	0.70	0.535
F value	0.44	1.97	1.73		
P value	0.666	0.265	0.358		

The Proteobacteria dominated in the soil sampled (mean relative abundance 56.30±10.05%) followed by Acidobacteria (19.21±7.27%, mostly Acidobacteria-6 (11.04±5.60%) and Firmicutes (7.83±5.26%, mostly Bacilli (6.37±4.87) (Fig. 1). The Betaproteobacteria (17.39±5.78%), Gammaproteobacteria (17.39±5.78%) and Alphaproteobacteria (17.39±5.78%) were the most dominant classes, while iii1-15 (10.72±5.53%), Acidobacteria, Xanthamonadales (7.78±2.52%) and Burholderiales

(7.42±2.72%) the most dominant orders. Phylotypes belonging to *Bacillus* (3.81±4.57%), *Halomonas* (3.08±4.79%) and *Rhodoplanes* (1.13±0.48%) were the most dominant genera, albeit with a large variations between the soil samples.

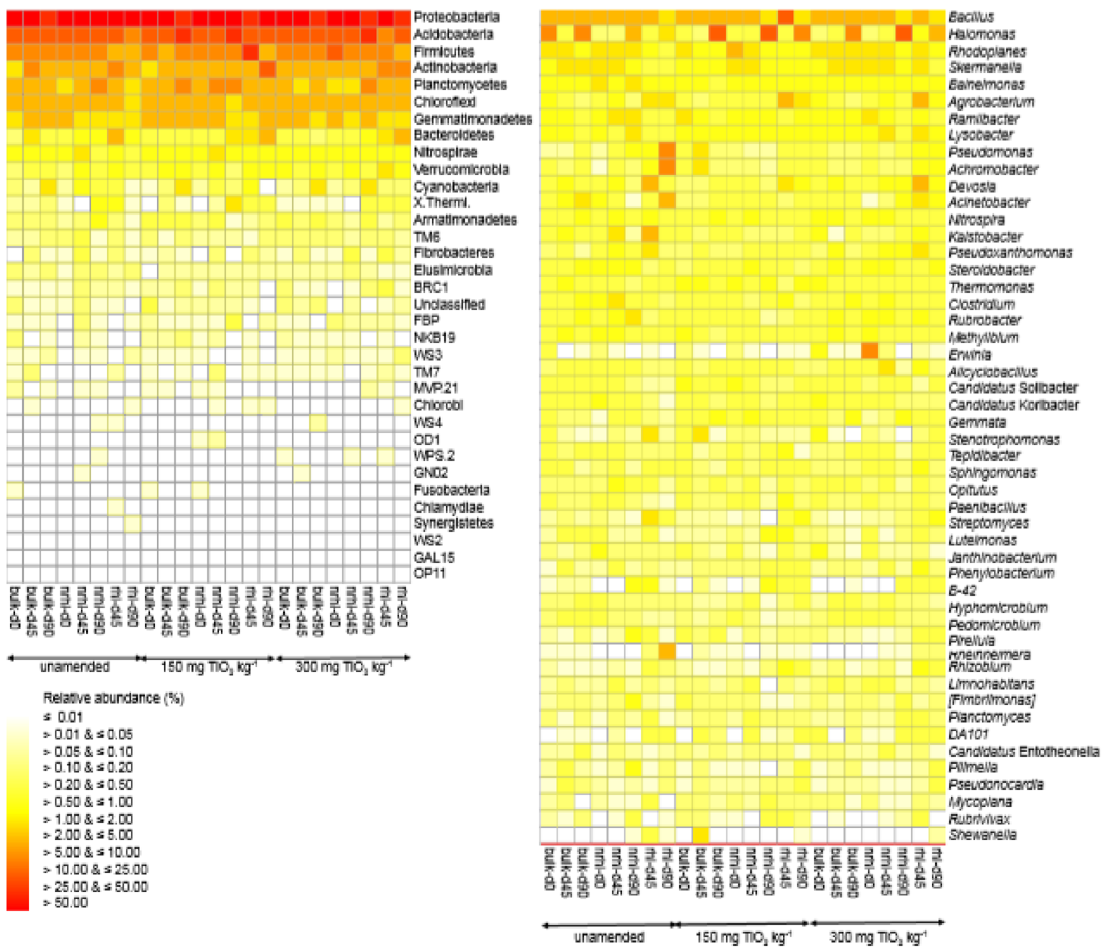

Fig. 1. Relative abundance (%) of bacterial phyla and 50 most abundant genera in a) unamended soil, b) soil amended with 150 mg TiO_2 kg^{-1} dry soil or c) 300 mg TiO_2 kg^{-1} dry soil. Soil not cultivated with bean plants (*Phaseolus vulgaris* L.) at day 0 (bulk-d0), day 45 (bulk-d45) and day 90 (bulk-d90), non-rhizospheric soil at day 0 (nrhi-d0), day 45 (nrhi-d45) and day 90 (nrhi-d90) and rhizosphere soil of bean plants at day 0 (rhi-d0), day 45 (rhi-d45) and day 90 (rhi-d90).

The PCA did not show a clear effect of the application of nanoparticles on the bacterial phyla in the bulk, non-rhizospheric and rhizosphere soil (Fig. 2). The PERMANOVA analysis confirmed the PCA, as the application of nanoparticles had no significant effect on the bacterial phylum community structure in the bulk, non-rhizospheric and rhizosphere soil or in soil in general (Table 3).

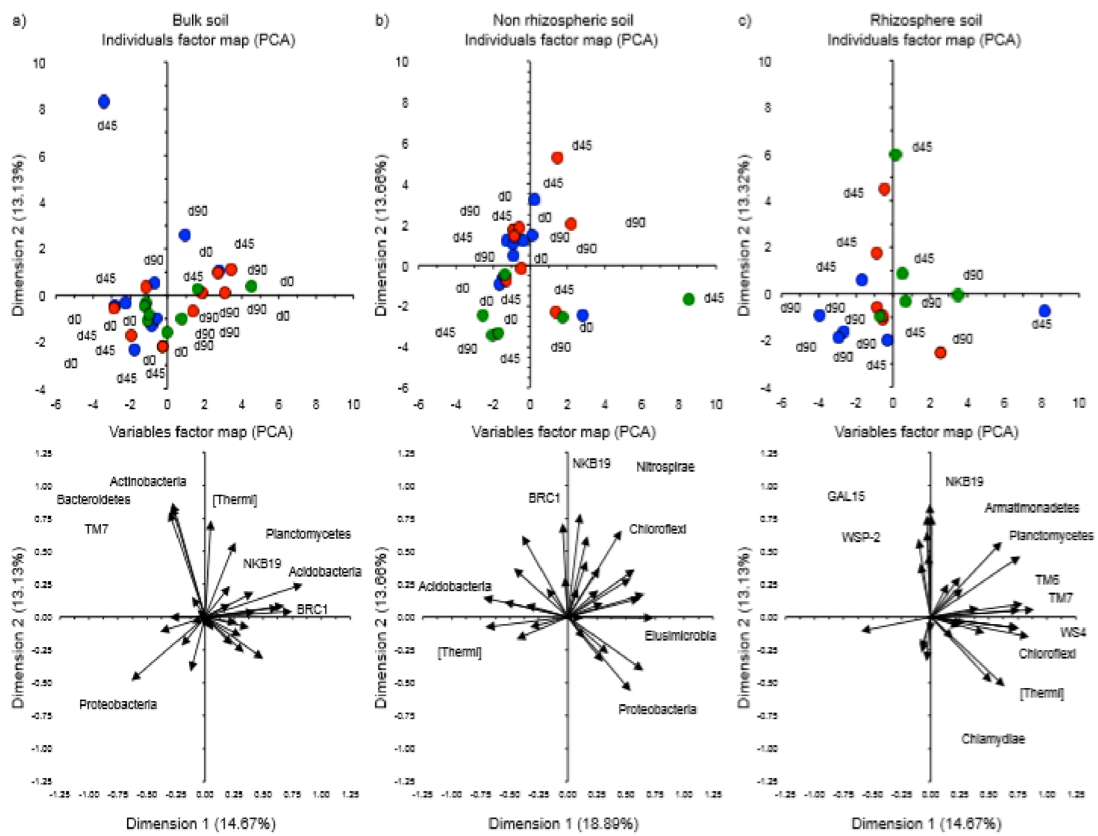

Fig. 2. A principle component analysis (PCA) with the relative abundance of bacterial phyla and in a) soil not cultivated with bean plants (*Phaseolus vulgaris* L.) or bulk soil, b) non-rhizospheric or c) rhizosphere soil of bean plants. Unamended soil (●), soil amended with 150 mg TiO_2 kg^{-1} dry soil and (●) and 300 mg TiO_2 kg^{-1} dry soil (●).

Time had a significant effect on the bacterial phylum community structure in the non-rhizospheric soil and the interaction of time and nanoparticles in the rhizosphere soil. Considering the 50 most abundant genera, the application rate of nanoparticles did not affect the bacterial community structure in the bulk, non-rhizospheric and rhizosphere soil, but time appears to change it especially in the non-rhizospheric and rhizosphere soil (Fig. 3). After 90 days, members of *Candidatus* Koribacter and *Planctomyces* were enriched in the non-rhizospheric soil and *Pseudomonas* in the rhizosphere soil. The PERMANOVA analysis confirmed the PCA, as the application of nanoparticles had no highly significant effect on the bacterial phylum community structure in the bulk, non-rhizospheric and rhizosphere soil or in soil in general, but time had a highly significant effect on it in the non-rhizospheric and rhizosphere soil (P<0.001) (Table 3).

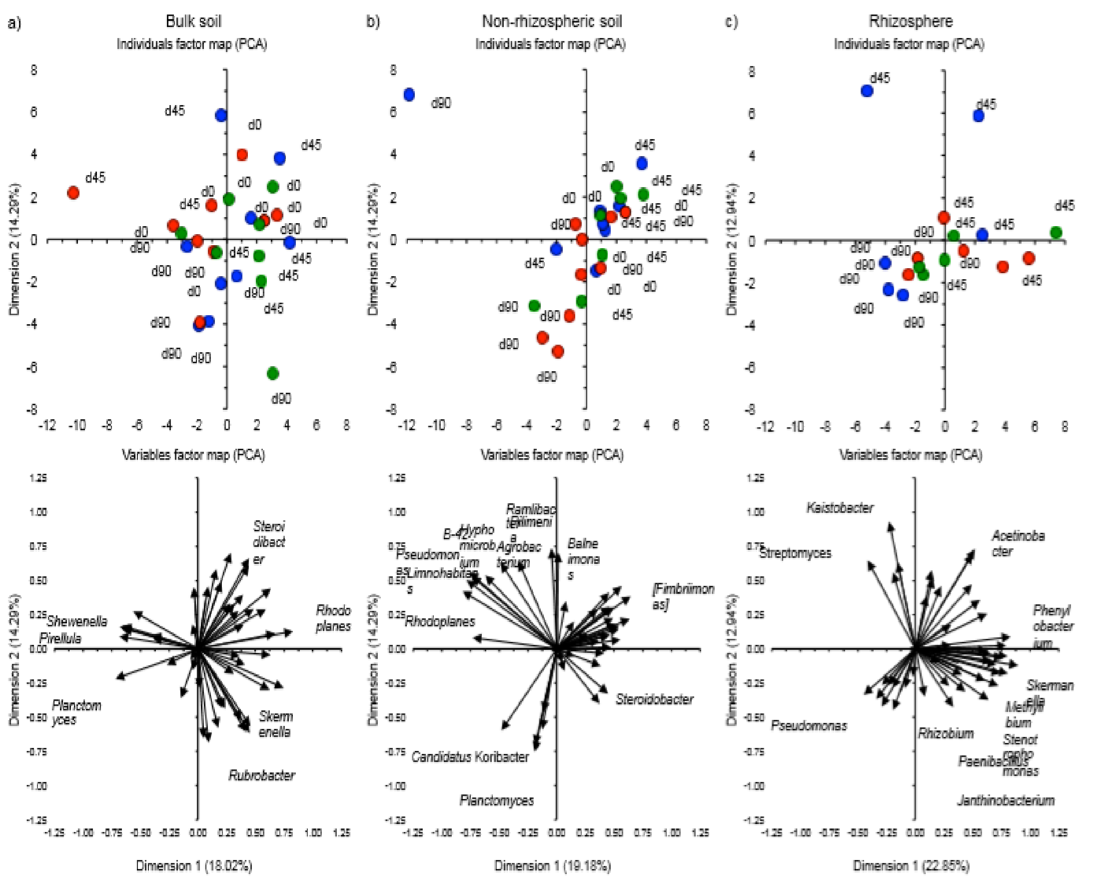

Fig. 3. A principle component analysis (PCA) with the relative abundance of the 50 most abundant bacterial genera and in a) soil not cultivated with bean plants (*Phaseolus vulgaris* L.) or bulk soil, b) non-rhizospheric or c) rhizosphere soil of bean plants. Unamended soil (●), soil amended with 150 mg TiO_2 kg^{-1} dry soil and (●) and 300 mg TiO_2 kg^{-1} dry soil (●).

Table 3. Permanova analysis
a) Effect of nanoparticles (0 mg TiO2 kg^{-1} soil), time (day 0, 45 and 90) and location (bulk, non-rhizospheric and rhizosphere soil) on the relative abundance of the bacterial phyla and genera.

	Phyla		Genera	
Factor	F value	P value	F value	P value
Nanoparticles (Nan)	1.50	0.196	1.16	0.279
Soil	5.62	<0.001	5.28	<0.001
Time	3.93	0.010	9.33	<0.001
Nan×Soil	1.56	0.162	1.57	0.060
Nan×Time	2.00	0.132	2.65	0.012
Soil× Time	3.52	0.006	2.97	<0.001
Nan×Soil×Time	3.88	0.003	1.54	0.077

b) Effect of nanoparticles (0, 150 or 300 mg TiO2 kg^{-1} soil) and time (day 0, 45 and 90) on the relative abundance of the bacterial phyla and genera in the bulk, non-rhizospheric or rhizosphere soil.

	Bulk soil				Non-Rhizospheric soil				Rhizosphere soil			
	Phyla		Genera		Phyla		Genera		Phyla		Genera	
	F value	P value	F value	P value	F value	P value	F value	P value	F value	P value	F value	P value
Nanoparticles (Nan)	0.22	0.929	0.64	0.740	0.14	0.952	0.92	0.447	2.70	0.082	2.01	0.043
Time	2.48	0.081	3.25	0.010	5.21	0.014	7.98	<0.001	3.07	0.056	4.03	<0.001
Nan×Time	0.39	0.782	1.97	0.077	1.71	0.158	1.95	0.105	5.01	0.012	1.68	0.105

The rhizosphere soil was clearly separated from the non-rhizospheric and bulk soil considering the bacterial phyla, but even more so considering the 50 most abundant bacterial genera (Fig. 4, 5). The rhizosphere in the soil not amended with TiO_2 was characterized by a larger relative abundance of Proteobacteria, in the soil amended with 150 mg TiO_2 kg^{-1} by a larger relative abundance of Actinobacteria, Bacteroidetes and Verrucomicrobia and in the soil amended with 300 mg TiO_2 kg^{-1} by a larger relative abundance of Actinobacteria, Bacteroidetes, TM7 and Verrucomicrobia compared to the bulk and non-rhizospheric soil (Fig. 4). Considering the 50 most abundant bacterial genera, the rhizosphere in the soil not amended with TiO_2 was characterized by a larger relative abundance of *Streptomyces*, in the soil amended with 150 mg TiO_2 kg^{-1} by a larger relative abundance of *Agrobacterium* and *Lysobacter* and in the soil amended with 300 mg TiO_2 kg^{-1} by a larger relative abundance of *Agrobacterium* and *Rhizobium* compared to the bulk and non-rhizospheric soil (Fig. 5). The effect of soil (bulk, non-rhizospheric and rhizosphere), time (day 0, 45 and 90) and their interaction on the bacterial community (phyla and genera) was mostly significant ($p < 0.05$) and often highly significant ($p < 0.001$) (Table 3).

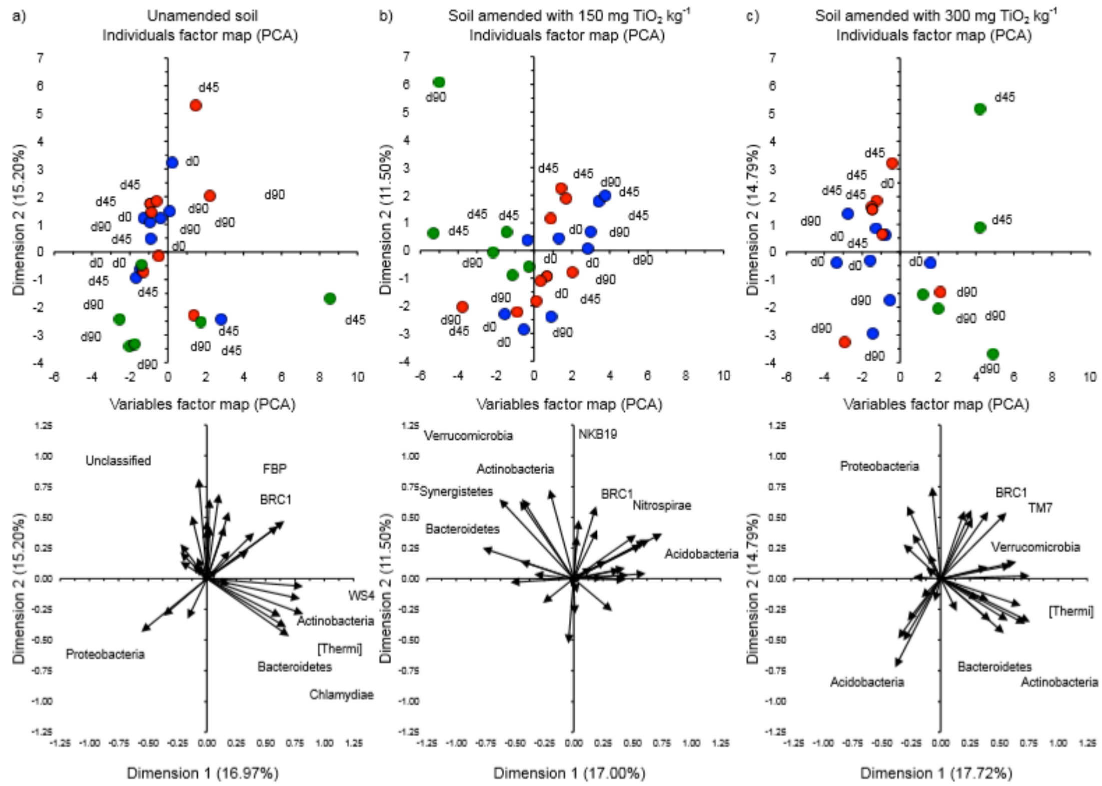

Fig. 4. A principle component analysis (PCA) with the relative abundance of bacterial phyla in a) unamended soil, b) soil amended with 150 mg TiO_2 kg^{-1} dry soil or c) 300 mg TiO_2 kg^{-1} dry soil. Soil not cultivated with bean plants (*Phaseolus vulgaris* L.) (bulk soil, ●), and non-rhizospheric (●) and rhizosphere soil (●) of bean plants.

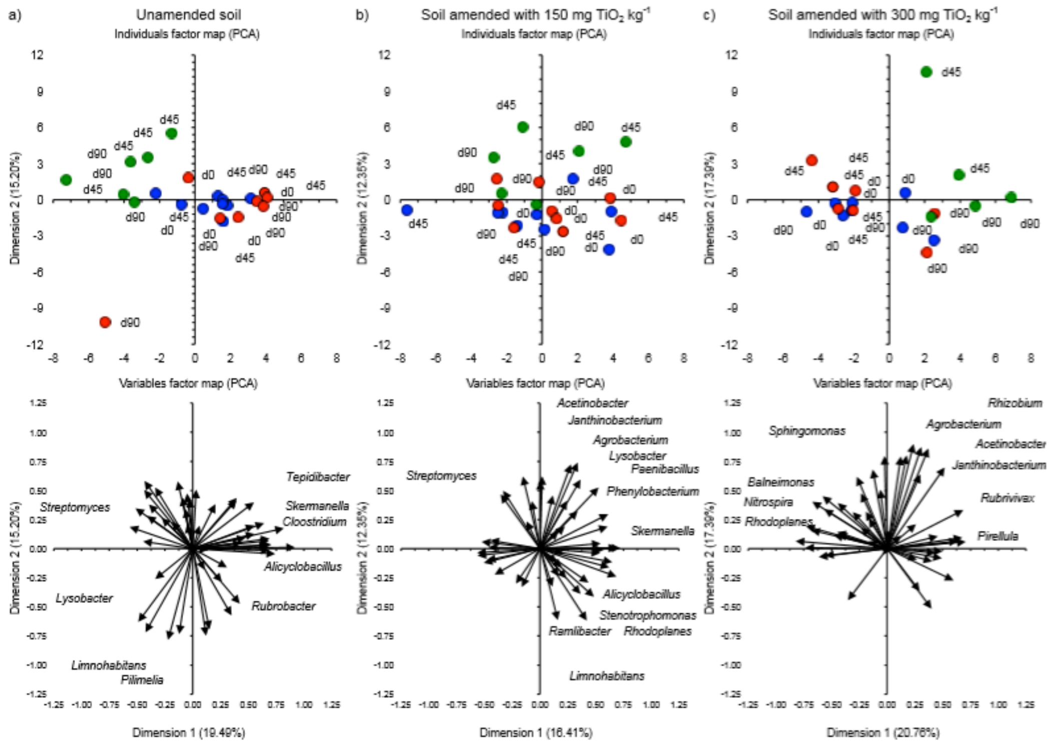

Fig. 5. A principle component analysis (PCA) with the relative abundance of the 50 most abundant genera in a) unamended soil, b) soil amended with 150 mg TiO_2 kg^{-1} dry soil or c) 300 mg TiO_2 kg^{-1} dry soil. Soil not cultivated with bean plants (*Phaseolus vulgaris* L.) (bulk soil, ●), and non-rhizospheric (●) and rhizosphere soil (●) of bean plants.

The CAP analysis did not separate the effect of different application rates of TiO_2 in the bulk, non-rhizospheric and rhizosphere soil considering the bacterial phyla (Fig. 6). However, the CAP analysis showed an effect of time on the most abundant bacterial genera, but not an effect of the TiO_2 application rate (Fig. 7). In the non-rhizospheric soil, for instance, the relative abundance of *Halomonas* was higher after 90 days than at the onset of the experiment (Fig. 7b).

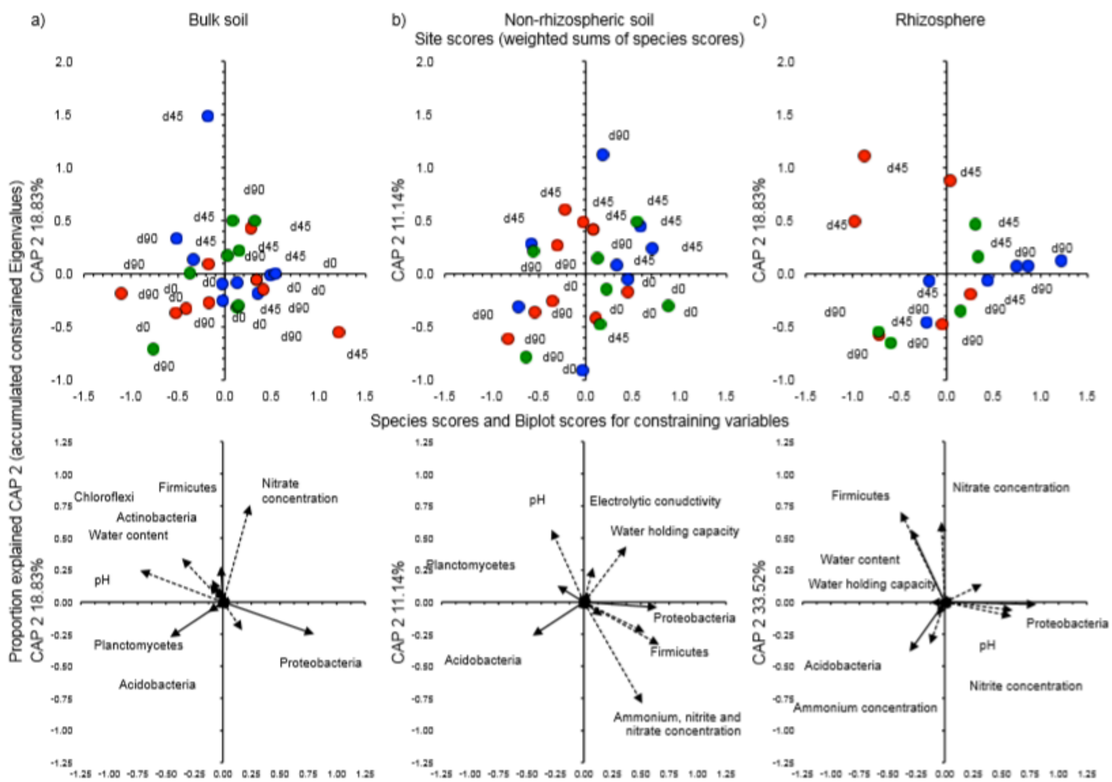

Fig. 6. A constrained analysis of principal coordinates (CAP) with the soil characteristics determined and the relative abundance of bacterial phyla in a) unamended soil, b) soil amended with 150 mg TiO_2 kg^{-1} dry soil or c) 300 mg TiO_2 kg^{-1} dry soil. Soil not cultivated with bean plants (*Phaseolus vulgaris* L.) (bulk soil, ●), and non-rhizospheric (●) and rhizosphere soil (●) of bean plants.

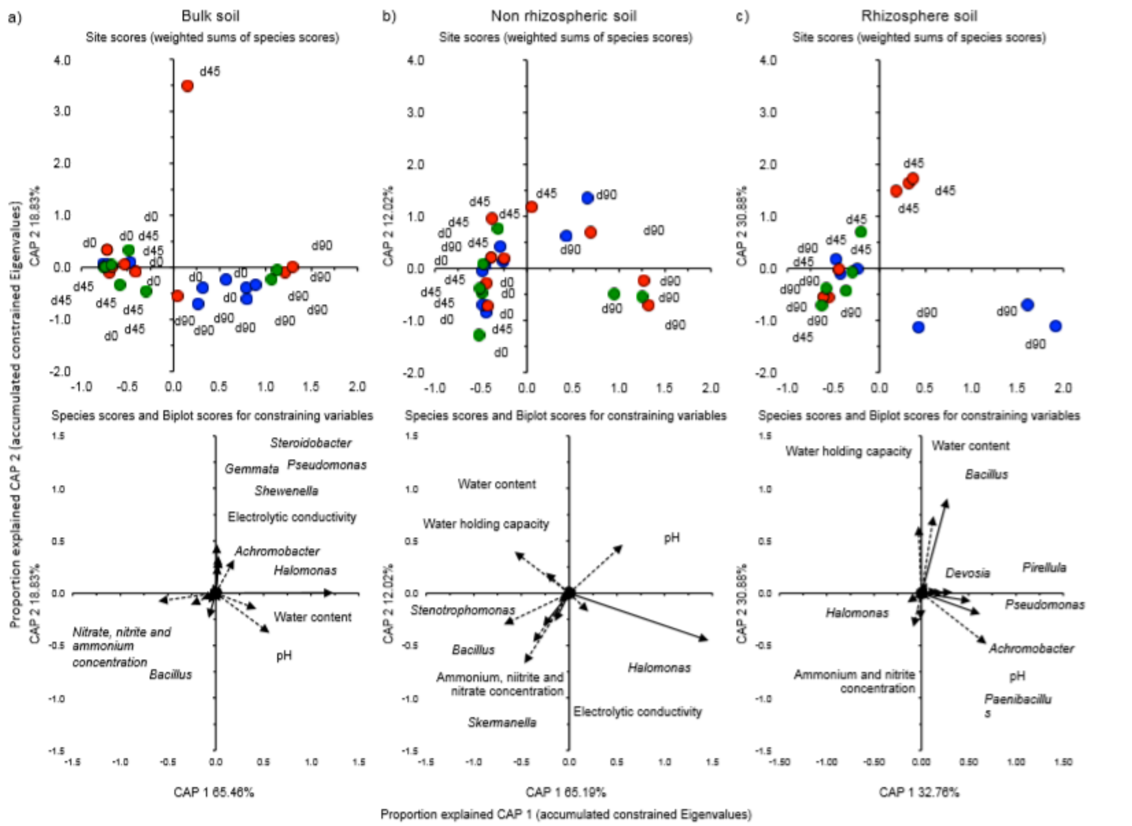

Fig. 7. A constrained analysis of principal coordinates (CAP) with the relative abundance of the 50 most abundant genera in in a) unamended soil, b) soil amended with 150 mg TiO_2 kg^{-1} dry soil or c) 300 mg TiO_2 kg^{-1} dry soil. Soil not cultivated with bean plants (*Phaseolus vulgaris* L.) (bulk soil, ●), and non-rhizospheric (●) and rhizosphere soil (●) of bean plants

Consequently, the factors and characteristics used in the random Forest analysis could explain the variation of only two bacterial phyla for > 20 % (Acidobacteria 22.98% and Fibrobacteres 20.75%) and two genera (*Acetinobacter* 21.48% and *Kaistobacter* 47.15%).

Discussion

The SPAD units of a plant leaf are correlated to their chlorophyll content. Gomez et al. (2011) measured SPAD units in leaves of common bean and they reported values between 40 – 45 SPAD units. The application of $nTiO_2$ had no effect on the chlorophyll content of the bean plants as reported by Medina-Pérez et al. (2018). They found that using $nTiO_2$ at 1 or 6 g L^{-1} in an irrigation solution did not increase the chlorophyll content of common bean plants. Gao et al. (2013), proved that nano-TiO_2 reduces the photosynthetic capacity of *U. elongata* seedlings. Hong et al. (2005) in their study provided evidence that the function of nano-TiO_2 is related to the activation of the photochemical reaction of chloroplast of spinach leaves (Spinacia oleracea L.) Gao et al. (2013) found that $nTiO_2$ reduced the photosynthetic capacity of woody plant *U. elongata* seedlings as these nanoparticles affect the activation of the photochemical reaction of chloroplast of spinach leaves (*Spinacia oleracea* L.) (Hong et al. 2005).

The effect of nanoparticles on plant growth can be both absent, positive or negative. The effect of nanoparticles depends on the concentration, composition, size, physical and chemical characteristics of nanoparticles, and the plant species (Ma et al. 2010), plant substrate i.e., soil, hydroponics or culture medium, and the time of exposure of nanoparticles on plants are also of singular relevance (Siddiqui et al. 2015; Rizwan et al. 2016). Titanium dioxide nanoparticles favourably alter plant physiological responses (Lu et al. 2002; Bao-shan et al. 2004; Zheng et al. 2005; Wang et al. 2011; Feizi et al. 2012; Wang et al. 2013; Jaberzadeh et al. 2013). Jacob et al. (2013) and Burke et al. (2015)

reported no effect of $$ on plant development as found in this study. Stampoulis et al. (2009) found no effect on seed germination of zucchini (*Cucurbita pepo* L.) when amended with four different nanoparticles (multiwalled carbon nanotubes [MWCNTs], Ag, Cu, ZnO and Si) grown in hydroponic solutions. Asli and Neumann (2009) studied maize *(Zea mays L.)* plants. They reported that the presence in the external water supplies of hydroponic maize seedlings of colloidal suspensions of $nTiO_2$ obtained from natural or industrial origin could lead to absortion at the cell wall surfaces of the primary root and consequent induced changes of cell wall pore size, water transport capacity, leaf growth and transpiration, they concluded that when maize plants were long term exposed to nTiO2 these developed an increased water transport capacity root systems, and this could represent a plant adaptation. Other studies found a negative effect of $nTiO_2$ on plant growth (Burke et al. 2014; Boonyanitipong et al. 2011; Kim et al. 2011; Seeger et al. 2009). Cao et al. (2016) investigated the impact of four different $nTiO_2$ on Pb accumulation in seedlings of rice (*Oriza sativa* L). They reported that $nTiO_2$ had no adverse effects on seedling growth and development, even when they applied 1000 mg kg^{-1}.

Bacterial community structure

Studies where pure cultures were used to investigate toxicity and adverse effects of different nanoparticles on bacteria cells. Nanoparticles might affect photocatalytic oxidation, cause DNA and membrane damage and generate reactive oxygen species (Brayner et al. 2006; Choi et al. 2008, Priester et al. 2009; Fan et al. 2014). Although there are several studies about soil microbial response to $nTiO_2$ (Ge et al. 2011; 2012; Shah et al. 2014; Burke et al. 2014-2015; Moll et al. 2017, Ge et al. 2014), there is no concensus about the interactions and effects of nanoparticles and the soil microbial communities (Johansen et al. 2008; Kumar et al. 2011). The study that closest resemble our investigation was published by Moll et al. (2017). They used high-throughput sequencing tools to analyze bacterial communities and found that the amount of nanoparticules applied to soil had litle effect in bacteria community. Ge et al. (2011; 2012) found an effect of $nTiO_2$ on the microbial community structure, but only when high concentrations were applied (> 500 mg kg^{-1}) and after 60 days of exposure (Ge et al. 2012). The effects of nanoparticles might depend on soil type (Frenk et al. 2013) and soil used in this study might have mitigated a possible effect of TiO_2. Ge et al. (2011) used a grasland soil and found a negative linear correlation between $nTiO_2$ amount and microbial community. In contrast, Xu et al. 2015, did not found an effect of $nTiO_2$ on the microbial community structure and they hypothesized that the water content of the soil might be a defining factor that the results can be attributed to the different water contents between dryland soils. They stated that when the water content decrease in soils, $nTiO_2$ gets closer to soil microbes and can be concentrated thereby enhancing a possible negative effect on the soil bacterial communities (Ge et al. 2013). It is known, that in drier soils, decreases the competition among species, resulting in an increased microbial diversity (Treves et al. 2003), as an direct effect, time of exposure could reflect a mixture of other factors like water stress, substrate competition, among others (Xu et al. 2015, Jośko et al. 2014, Ge et al. 2013). Time of exposure to the nanopartciles is another factor that might determine a possible effect of on the microbial community. Ge et al. (2011; 2012) reported a higher effect after 60 days than after 15 days of exposure (Ge et al. 2011; 2012). The crystal structure of nanoparticle is another factor that could potentially affect the soil physicochemical characteristics, and thus affect the microbial communities. (Moll et al. 2017, Aminedi et al. 2013).

Moll et al. (2017) studied the microbial community in the soil. They investigated the changes in the structure of bacterial and fungal colonies in soil where wheat plants (*Triticum aestivum L*) were grown amended with 1, 100 or 1000 mg $nTiO_2$ kg^{-1} and found no change in the prokaryotic α-diversity when compared to the control treatment, and the results are different to our study but they did not specify if soil was rizhosferic. In contrast to our study, $nTiO_2$ concentration significantly altered the community structure of bacteria communities. Burke et al. (2014) using soybean (*Glycine max L.)* and maize *(Zea mays L.)* reported that the response of soil microorganism to $nTiO_2$ might be affected by the interactions between NPs and their root exudates. Ge et al. (2014) found that bacterial communities were affected differently by NPs in uncultivated soil or soil cultivated with soybeans. The mechanisms of how plant exudates, bacteria and engineered nanoparticles interact with each other are still unknown (Xu et al. 2018; Moll et al. 2017).

In contrast with other studies that stated that nanoparticles affected bacterial symbiotic N_2 fixation in soybean (Ge et al. 2014), in our experiment the relative abundance of *Agrobacterium* and *Rhizobium* was larger in the rhizosphere of the common bean (*Phaseolus vulgaris* L.) amended with 300 mg kg^{-1} than in the bulk, and non-rhizospheric soil. Ge et al. (2011) found that nano-TiO_2 and nano-ZnO affected bacterial taxa associated with nitrogen fixation (the order Rhizobiales), methane oxidation (the family Methylobacteriaceae) and recalcitrant organic compound decomposition (families

Sphingomonadaceae and Streptomycetaceae). Ge et al. (2014) found that soybean plant exudates could mitigate nano-ZnO toxicity towards bacteria by ion sorption thereby reducing Zn bioavailability. The authors suggested that the introduced carbon by root exudates, could lead to a protective effect, such as the formation of chelates that could sequestering toxic ions. Gorczyca et al 2018, studied the bacterial community conducted in rhizoplanes of wheat ***(****Triticum aestivum L)* and flax *(Linum usitatissium L.)*, and they found that the community of Pseudomonas and Bacillus spp. was stimulated by $nTiO_2$, they concluded that response of monocot (wheat) and Dicot(flax) growth form plants to the $nTiO_2$ was different, and the rhizoplane microbiome is dependent on the species of plant, and that the bacteria found in the communities are sensitive to $nTiO_2$ in diferent degree.

The most abundant phyla were Proteobacteria, Acidobacteria, and Firmicutes, which occurs often in soil (Ge et al. 2013; Ge et al. 2014; Burke et al. 2014; 2015; Cao et al. 2016). A recent study by Asadishad et al. (2018), found that Gammaproteobacteria, Actinobacteria, and Firmicutes were more resistant to addition of metal ions and nanoparticles (CuO_2, ZnO_2, Ag, TiO_2). However, $nTiO_2$ applied at 100 mg kg^{-1}, did not significantly affect the microbial community composition after 30. Ge et al. 2014 found that 0.5 g nZnO kg^{-1} soil significantly increased members of species such as *Rhizobium* and *Sphingomonas*, but decreased phylotypes belonging to *Ensifer*, Rhodospirillaceae, *Clostridium* and *Azotobacter*.

Conclusion

In this study application of 0.15 or 0.30 g $nTiO_2$ kg^{-1} did not affect the development of common bean plants. The amount of $nTiO_2$ applied did not alter the bacterial community structure in the bulk, non-rhizospheric and rhizospheric soil. The time of exposure had significant effect, in the non-rhizospheric and rhizospheric soil. The rhizospheric soil was clearly separated from the non-rhizospheric and bulk soil considering the bacterial phyla, but even more so considering the 50 most abundant bacterial genera. These findings need to be consider regarding to the use, disposal, or application of TiO_2 on agricultural soils, especially in long-term studies.

Systematic long-term studies in agriculture land sites should be carried out to understand how the interactions between nanoparticles and soil microorganisms are.

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ANEXOS

Table S1. Characteristics of titanium dioxide nanoparticles applied to common bean (*Phaseolus vulgaris* L.) cultivated in the greenhouse for 90 days.

Characteristics	TiO_2 Nanoparticle
Chemical formula	TiO_2
Color	White
Density (g/cm^{-3})	4.23
Molecular weight	79.87
Fusion point °C	1843
Crystalline phase	Anatase
Particle size	Less than 50 nm
Crystallographic system	Hexagonal
Magnetic properties	Weakly ferromagnetic

Table S2. Description of treatments applied to the arable soil.

Amount of nanoparticles applied	Plant cultivated	Samples taken
0 mg TiO_2 kg^{-1} dry soil		Day 0, 45 and 90
0 mg TiO_2 kg^{-1} dry soil	Bean plant	Day 45 and 90
150 mg TiO_2 kg^{-1} dry soil		Day 0, 45 and 90
150 mg TiO_2 kg^{-1} dry soil	Bean plant	Day 45 and 90
300 mg TiO_2 kg^{-1} dry soil		Day 0, 45 and 90
300 mg TiO_2 kg^{-1} dry soil	Bean plant	Day 45 and 90

Time	Treat ment	WHC(g.kg)		WC%	EC (dS m^{-1})		WC		pH		Nitrate(NO_3^-)		Nitrite (NO_2^-)		Ammonium(NH_4^+)	
45	1	839.61±32.26	**e**$^{\Sigma}$	21.03±5.53	1.76±0.37	**a**	210.27±55.32	**a**	7.91±0.18	**ab**	9.49±6.58	**ab**	0.3±0.01	**a**	2.09±0.36	**b**
45	2	676.84±43.25	**cd**	26.43±13.57	1.62±0.52	**a**	264.33±135.74	**a**	7.95±0.22	**ab**	3.49±3.67	**ab**	0.17±0.03	**a**	1.54±0.24	**ab**
45	3	643.02±24.43	**cd**	24.76±1.26	3.09±0.61	**b**	247.6±12.58	**a**	7.78±0.18	**a**	10.02±4.26	**ab**	0.18±0.03	**a**	1.47±0.18	**ab**
45	4	629.46±26.84	**bcd**	25.73±2.12	2.48±0.61	**ab**	257.33±21.22	**a**	7.85±0.14	**ab**	12.57±4.92	**b**	0.19±0.03	**a**	1.42±0.02	**ab**
45	5	658.89±34.33	**cd**	18.45±0.26	1.54±0.22	**a**	184.53±2.61	**a**	7.86±0.21	**ab**	6.56±0.84	**ab**	0.25±0.01	**a**	1.4±0.22	**ab**
45	6	625.01±39.47	**bcd**	23.26±4.22	2.23±0.1	**ab**	232.57±42.24	**a**	7.86±0.04	**ab**	12.51±3.24	**b**	0.24±0.05	**a**	1.27±0.14	**ab**
90	1	593.74±63.16	**abc**	18.27±0.47	1.76±0.37	**a**	182.7±4.68	**a**	8.11±0.23	**ab**	1.77±0.33	**a**	0.18±0.09	**a**	2.12±0.27	**b**
90	2	516.65±9.58	**ab**	20±1.73	1.62±0.52	**a**	200±17.32	**a**	7.97±0.1	**ab**	1.73±0.59	**a**	0.26±0.08	**a**	1.67±0.21	**ab**
90	3	616.17±3.57	**abcd**	25.58±1	3.09±0.61	**b**	255.77±9.99	**a**	8.07±0.23	**ab**	5.9±1.13	**ab**	0.16±0.03	**a**	1.34±0.34	**ab**
90	4	714.66±51.14	**d**	25.33±1.53	2.48±0.61	**ab**	253.33±15.28	**a**	8.11±0.1	**ab**	10.57±2.99	**ab**	0.2±0.02	**a**	1.44±0.57	**ab**
90	5	597.53±20.02	**abc**	18.33±3.21	1.54±0.22	**a**	183.33±32.15	**a**	8.32±0.2	**b**	4.58±0.9	**ab**	0.23±0.11	**a**	1.64±0.44	**ab**
90	6	504.02±62.92	**a**	26.25±0.67	2.23±0.1	**ab**	262.47±6.65	**a**	8.15±0.08	**ab**	4.78±0.82	**ab**	0.18±0.02	**a**	1.09±0.18	**a**

Table 3S. Soil dynamic characterization

Σ Values with the same letter within the columns are not significantly different ($P < 0.05$).

WHC (Water holding capacity), WC%(water content percentage), EC (Electrolytic conductivity). T6: Dry soil not contaminated with nanoparticles, without plant; T5: Unpolluted soil plus plant1 (dry soil),T4: Soil contaminated with 0.30g kg-1 (dry soil),T3: Soil contaminated with 0.15g kg-1 (dry soil), without plant,T2: Soil contaminated with 0.15g kg-1 (dry soil), with plant; T1: soil contaminated with 0.30g kg-1 (dry soil), with plant.

10.2 ETAPA DE INVESTIGACIÓN DOCUMENTAL

10.2.1 Artículo 3. Remediating polluted soils using nanotechnologies: Enviromental benefits amd risks.

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Review

Remediating Polluted Soils Using Nanotechnologies: Environmental Benefits and Risks

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Abstract

Since engineering nanoparticles (ENP) have been developed for using in industry and human commodities, is common to find their wastes and by-products from industrial chemical reactions, and it is also possible to find incidental nanoparticles in the environment. Currently, the remediation of polluted soils using nanotechnologies has become an emerging area with a huge potential to improve the performance of traditional remediation technologies. However, environmental concerns have also emerged regarding human and environmental health when nanotechnologies are released to ecosystems. The goal of this manuscript is to highlight the environmental benefits and risks that arise when nanotechnologies are used to remediate polluted soils. We searched Web of Science and Scopus in order to get latest updated information and patents pertaining to developments in the field of nanotechnologies for decontaminating soils. It has been determined that soil nanoremediation has some advantages, but it also has some disadvantages related to the final disposal of nanoparticles, nanomaterials, or nanodevices. Will some nanotechnologies be our pitfall? Nanoparticle toxicity has to be assessed and the standardization of techniques should be set by scientists and decision-makers worldwide. Cutting-edge knowledge regarding the use of nanoparticles to decontaminate soils has to move forward, but environmental quality, human health, and social welfare should also be ensured.

Keywords: ecological risk, engineering nanoparticles, environmental concerns, remediation, soil pollution, sustainability and social welfare, sustainable development

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Introduction

Plants perform many ecological functions in their environments, and they shape the life in the environment where they live. Living things in the world are directly or indirectly dependent on plants [1-6]. The ability of plants to fulfil their functions primarily depends on the availability of appropriate climatic and edaphic conditions [6-9]. Therefore, soil is a necessary condition for plant existence.

Soil is defined as the part of the solid earth that has been altered by the loosening of the earth, humus formation, and chemical decomposition, and by the transportation of humidification and chemical decomposition products [7, 10-19]. However, when it is examined in detail, soil is a complex structure and the biological and biochemical processes in it are the basis of the terrestrial ecosystems [7, 8, 10-19]. In this respect, it is imperative to examine health changes of the soil and to determine its relationship with the plant. Also, both improving the soil quality throughout soil conservation and remediation technologies, and reducing the conditions that jeopardize soil quality are two critical points to shape the sustainability of soils [20-25].

Currently, advancements in the fields of nanoscience and nanotechnology have delivered myriad possibilities for consumer product applications. Many of these products have already migrated from laboratory working tables toward store shelves and e-commerce websites. However, research regarding nanoparticles, nanomaterials, or nanodevices is still ongoing regarding their potential effect on human and environmental health [20-21].

Also, new areas of knowledge have emerged along with nanoscience and nanotechnology such as nanotoxicology, nanobiotechnology, nanoremediation, etc. However, cutting-edge knowledge regarding the use of nanoparticles to decontaminate soils is being built right now worldwide. It is well known that knowledge regarding nanoremediation has to move forward, but it is also well known that this huge challenge requires the participation of scientists from many areas of knowledge [22-23]. It has been reported that nanoparticles might increase polycyclic aromatic hydrocarbon (PAH) dissipation in a polluted soil when it is amended with wastewater sludge, polyacrylamide, and nanoparticles [23-25]. Besides, the use of nanotechnologies to decontaminate soils has frequently been published during the current year [26-28]. However, the development of the appropriate use of nanotechnologies for remediating polluted soils has to be achieved as soon as possible in parallel with a comprehensive understanding of the human and environmental risk-benefit balance [29].

Soil contains many kinds of organic and inorganic particles in the nanoscale or colloidal range, i.e., <100 nm [30]. However, a lot of nanoparticles, nanomaterials, or nanodevices have been used to dissipate soil pollutants notwithstanding the interactions of nanoparticles with the soil environment that have not been well studied, i.e., the movement, fate, and bioavailability of nanoscale materials into soil matrix are still unknown. In addition, the increasing entry into soil of engineered and anthropogenic nanoparticles has raised concerns about their potential adverse effects on human, animal, or ecosystem health.

The goal of this review is to highlight the environmental benefits and risks that emerge when nanotechnologies are used to remediate polluted soils. Therefore, this manuscript shows an updated discussion about the nanoremediation of polluted soils and its human and environmental risks or benefits.

Soil Environment

The environment of soil is a complex system from several points of view. For example, the soil matrix is a tri-phasic system, i.e., it has solid, liquid, and gas phases or states. Additionally, there are biotic and abiotic interactions, the biotic interactions by microorganisms such bacteria, virus, fungi, protozoa, and amoebas, mainly, and as multicellular organisms are nematodes, arachnids, mites, earthworms, etc. The abiotic interactions are by mineral elements such as alkaline and transition metals, particularly.

Soil microorganisms play important roles in plant growth and agroecosystem (they are involved in soil ecosystem, in the decomposition of organic residues, and they are the key to driving nutrient cycling in soils, such as biogeochemistry cycling of carbon, nitrogen, phosphorus, and potassium, mainly). The extensive use of nanoparticles (NPs) will increase their concentration into the soil and consequently their environmental effects and ecological risks [31], by manufactured NPs for products with a wide industrial, commercial, medical, and agricultural applications [25, 32]. Some metal or metal oxide NPs have been found to be highly toxic toward soil microorganisms and to have a high impact on soil microbial species diversity [24, 32]. However, there are reports about beneficial effects of some NPs, as stated by He et al. [32], who reported that the changes in abundances of bacteria, eukaryotes, and ammonia-oxidizing bacteria measured by real-time polymerase chain reaction (Real-Time PCR), also known as quantitative polymerase chain reaction (qPCR), studying the effects of metal or metal oxide nanoparticles on soil microbial metabolic activity and the key ecological functions. It was found that AgNP (at 0.1, 1 and 10 mg kg^{-1} soil) amendments decreased soil microbial metabolic activity, nitrification potential, and the abundances of bacteria and ammonia-oxidizing bacteria. On the opposite, it was found that FeO-NPs had positive effects on soil microbial metabolic activity (at 1 and 10 mg kg^{-1} soil) and soil nitrification potential (at 0.1 and 1 mg kg^{-1} soil) [32].

We observe that concerns are about the synthesis and production of NPs (unpublished data), but not on the toxicological, environmental, exposure, or disposal effects on humans, animals, and plants. So, the view about the extensive application of NPs under the non-regulated condition of many applications must be a concern.

Nanoscience and Nanotechnology as Useful Tools in Agriculture

Nanotechnology is a multidisciplinary science research area that basically works in the design, characterization, fabrication, and application of structures and constituents, and is created by the controlled size manipulation and shape at the nanometer scale (atom and molecular, less than 100 nm) producing structures, components, and systems with at least one feature or new characteristic or higher property [33]. These new materials are engineered intentionality looking for advantages over traditional materials. The nano-sized particles have reached a big amount scale production, estimated to be 260,000-309,000 metric tons in the 2010 and about 8-28%, 0.4-7%, and 0.1-1.5% were calculated to end up in environmental containers: soil, water bodies, and atmosphere, respectively [34].

According to the report published by FAO in 2013 on the state of the art of nanotechnology in food and agriculture, research was conducted for ten years seeking to achieve sustainability and solutions to environmental problems. Such investigations focus on: the smart release of active ingredients (disease management and crop protection), minimizing the loss of nutrients in fertilization and increasing performance, and producing bio-nano compounds from traditional crops [35].

The need to increase food production is projected to reach 9.9 billion people by 2050 [36]. A growing population requires the optimization of resources (soil, water, inputs) and the conditioning of damaged soils for agriculture uses. Declining oil reserves will generate a transition to the production of energy crops gradually. As a result of FAO in the 2009 forum of experts, "How to feed the world in 2050," it will be necessary to increase grain production by 70% by 2050. Nanotechnology can supply tools in modern agriculture and become useful in the solution of future problems of food and energetic demand with a sustainable approach (Fig. 1).

Our knowledge about the interactions of ENMs with soil is very limited, and because of the complexity of this system, there is still a long way to completely understanding the behavior of anthropogenic nanoparticles. The last fifteen years of soil studies are encouraging in transcendental issues: improving fertility, reducing degradation, attenuation or degradation of contaminants, and developing nutrient and pollution sensors [37, 38].

The development of nanocomposites and nanoencapsules suggests that controlling amounts of active ingredients needs to be taken up in a stable form throughout crop growth, avoiding overdoses, and reducing input and waste [39]. These active ingredients can be fertilizers [40, 41], herbicides [42-44], plaguicides [45, 46], or growth promotors [47], and their rationalization and control of the amount of application could be effective in reducing the overall costs of cleaning up highly contaminated places by eliminating the need for treatment and disposal of contaminated soil [48].

About improving and maintaining soil conditions, there are published on the web several reviews about applications of nanomaterials that are potentially useful [39, 49]. Progress has been documented in retaining nutrients since it is known that only a small percentage of the fertilizer applied is used by crops, the rest is lost by washing, processing or mineral retention, and the use of nanofertilizers allows the nutrient movement in the rhizosphere, improving composition and doses. Today it is possible to design NPs or nanoscale vehicles to reach the roots and enhance the uptake of beneficial molecules. These vehicles could also look for specific soil particles and repair damage [50].

Bin Hussein et al. [51] reported on utilizing zinc and aluminum hydroxide-based composites as a coating to slow the liberation of nutrients. Kottegoda et al. [52] encapsulated urea hydroxyapatite nanoparticles in wood, where they liberated nitrogen during 60 days versus 30 days of commercial fertilizer. There is a list of

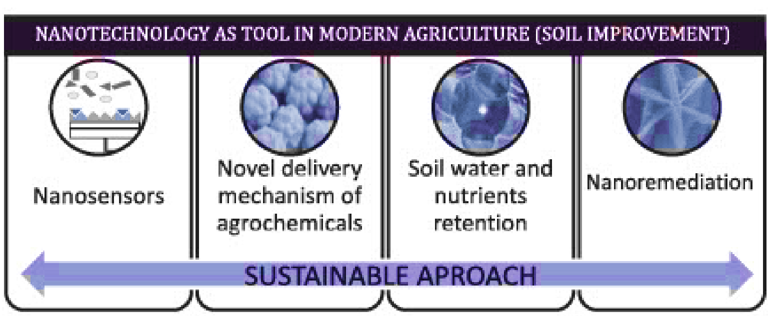

Fig. 1. Technological advances aiming to improve soil quality and reduce its pollution through nanotechnological applications .

patented products, one of them based on a mixture of nitrogen, phosphorus, potassium (NPK), micronutrients, mannose, and amino acids designed for grain crops [53]. The loss of nitrogen by leaching is well known, which is the cause of eutrophication of water; this problem was less present when fertilizers were coated by nanomaterials like plastic-starch mixtures of composites [54].

Water retention of nanomaterials has been developed in nanoclays, nanozeolites, and nanohydrogels [55]. Sekhon [56] showed a complete review of them and their novel properties. Nanoclays, made of polyacrylamide polymer, is a nanocomposite that presents high water absorbency and water retention when coated with zinc. This is an important characteristic because they could be applied to rain-fed crops [57]. Recent research on the present year by Mahfoudhi and Bouf [58] designed nano-hydrogels based on cellulose nano-fibrils (CNFs) and polyacrylic acid-co-acrylamide. The obtained structure caused the system to release urea simulating a fertilizer. This last report shows the combined properties of nanomaterials to enhance soil conditions. Kottegoda et al. [59] drank hydroxyapatite nanoparticles (obtained from H_3PO_4) between spaces of clay platelets and they achieve a slow release of phosphate, the same authors included modified cellulose for the same protective function. Liu and Lal [60] produced synthetic apatite nanoparticles as the form of phosphorus slowly loaded for soybean plants (*Glycine max* L.).

Mesoporous silica (MSN) are used to load pesticides, this coat protects the active ingredient (avermectin) from photodegradation, and dosified slowly thus they remain active longer [61]. Some nanomaterials are useful in crop protection and eventually become "soil friendly" due to their biodegradability. Khot et al. [62] was encapsulated inside a mixture of chitosan and alginate with two active substances (nano-imidacloprid in combination with Ag/TiO_2) for plague control. As a result, the residues of the formulation were degraded in the soil after eight days of application. Zhao et al. [63] presented a complete overview about the bio-nanocomposite, and the proposal has the advantages of utilizing biodegradable polymeric matrices based on proteins or starch in order to protect fertilizer formulas and nanobioplastics production. The application of biochar has shown interesting results, including soil amendment and sorption of several undesirable residues [64, 65].

In respect to the nanosensors, there are advances and improved features compared with the common sensors. The nanosensors are made for sensing 100 nm or fewer dimensions. Nanotubes, nanoparticles, nanocrystals, or nanowire send a signal in response to the presence of other composites of similar size. The big surface reaction of nanomaterials gives back a rapid reaction, enhancing the sensitivity of the detection system; installing nanosensors in fields allows the farmer to know in real time the conditions of soil and very early detection of potential problems such as water deficit and soil nutrient demand. It could be an advantage enhancing precision farming in the next years in order to improve the reactions in front of agronomic challenges [24, 25, 66].

Natural and Anthropogenic Occurrence of Nanosized Materials in Soil

Nanoparticles (NP) are considered to be the building blocks for nanotechnology, and refer to particles with at least one dimension < 100 nm [22, 24, 25, 67]. On the other hand, the nanomaterials (NM) are defined as engineered materials with a least one dimension in the range of 1-100 nm [22, 68]. Soils are a repository of many engineered and natural nanoparticles prevenient of many industrial and environmental applications, and this has originated discussions concerned its effect on biological systems, especially on human health and about its role on geochemical processes [23, 69] and impacts on the ecosystems [25, 70].

Nanoparticulate Materials in the Environment

As it was said before, these nanomaterials are a complex mixture of natural and anthropogenic nanostructures [71]. Nanoparticles had reached the environment before the field of nanotechnology emerged. The most important sources of natural nanoparticles have been present as geogenic dust [72], volcanic soot, and carbonaceous particulate matter [73], and sub-products of combustion processes such as power generation and transportation [74], and erosion [75]. Since the nanoparticles have been developed for use in industry and human commodities, it is common to find wastes and sub-products from industrial chemical reactions [76], wastewater treatment plants [77], and landfill lixiviation [78], among other activities.

The presence of the nanomaterials is not only associated with their natural origin; it is also possible to observe the non-intentional release due to manufacturing or transportation [79]. Because of the diversity of the nanotechnology applications, the nanoparticles may enter the environment through many pathways, for instance emissions to the atmosphere may result in deposition to soils and water, the use or nanotechnologies for remediating polluted soil, it may also enter as a result of the wastewater treatment, as a sub-product of water treatments sewage sludge or accidentally during spills. Despite knowledge about the release pathways, some nanoparticles present in the environment are still unknown [80].

In most cases the dispersion medium of nanoparticles that come in close contact with man of other living components is air or water, therefore the soil is the main receptor of most of the either natural and anthropogenic nanoparticles via direct release or because of the deposition of nanoparticles [81]; this complex multiphasic matrix releases the nanomaterials to plants and animals, and greatly affects human health [82].

Natural Nanoparticles

According to Lungu et al. [83], earth, cosmic, and weather-dependent phenomena on the planet produce particulate matter that is lifted in the air through volcanic eruptions, air currents generated by storms or strong winds, the disintegration of meteorites entering the atmosphere, or the accumulation of cosmic dust. The evolutionary development of hominids has been accompanied by the presence of natural nanominerals and mineral nanoparticles [84].

Humic and Fulvic Acids

The particles belong to the clay fraction in the soil and have been classified as particles smaller than 2 micrometers; however, it is possible to identify colloidal particles in size range of 1 to 100 nanometers, allowing for the inclusion of this fraction to the nanosize scale.

As a ubiquitous component in soil, the organic matter may influence greatly some properties of the nanoparticles such as surface speciation and electric charge [85], affecting their aggregation/deposition properties. Their biological importance is based on structural support for microbial communities and its function as a nutrient provider [86]. On the other hand, the fulvic and humic acids participate as acceptors and donors of electrons for the biodegradation of contaminant compounds [87]. In some cases, they are involved in processes of contaminant transportation and can enhance the chemical degradation [88-90]. The mobilization of NPs in soil is driven by its interaction with the organic matter, and it can affect superior organisms such as plants, animals, and finally humans [91].

Generic Geogenic Oxides

The primary and permanent reservoirs of nanoparticles and nanomaterials are deserts. Shi et al. [92] reported that about 50% of the minerals in aerosols in world air come from deserts. Although the composition is variable, the most important group of geogenic nanoparticles are formed by oxides, hydroxides, and oxyhydroxides of metallic elements such as Al, Fe, and Mn, which were formed by weathering of silicates and microbial pathways [93].

Some special characteristics are related directly to the origin, and its distribution in the environment is variable. For example, the aluminum nanostructures can be found in soil as gibbsite and boehmite, generated by geological processes. The manganese nanoparticles are formed during bioprocesses in soil bacteria and fungi [94]. Also, the iron hydro oxides are among the most abundant natural nanoparticles in soil, developing an important role in the process of nutrients absorption, and acting as exchangers of molecules due to its electrostatic charge [30].

Anthropogenic Nanoparticles

All the human activities have an impact on the environment. The development of new materials and particles for diverse applications has driven into a new era: the nanoscale dimension. The anthropogenic sources of nanoparticles and nanomaterials are classified as primary due to mineral exploitation and the secondary given by industrial activities (stationary or mobile sources) [83, 95].

The presence of primary nanoparticles is localized in places with activities such as fossil fuel exploitation, ferrous, and non-ferrous mineral extraction and exploitation of natural materials for construction. The nanoparticles prevenient from primary sources are not as harmful as the nanoparticles prevenient from secondary sources.

Carbon Nanotubes

Probably, the most relevant example is given by graphene, which has an excellent thermal and electrical conductivity and is released to the environment as a result of the discharge of the materials containing this material (plastics, electrodes, sensors, automotive components). It has been reported that the nanomaterial may behave differently in the environment and it could affect the biogeochemical and microbial dynamics in soil [96].

Engineered Metallic Oxides

Most of the metallic nanoparticles have been developed for the cosmetic sector [97], catalyzers in industrial processes [98], medical diagnosis [99], delivery of drugs [100], and bioremediation of polluted soil and water [101, 102].

Oxide metallic nanoparticles have been elaborated upon as both individual oxides (ZnO, TiO_2, CeO_2, CrO_2, MoO_3, and Bi_2O_3) and binary oxides ($BaTiO_3$, $LoCoO_2$, and InSnO) [103, 104], and according to their composition, variable adverse effects in soil have been reported.

Inventory of Nanowastes in the Environment

Despite the commercial and technological importance of NP and NM, its presence – natural, intentional, or accidental – in the environment is still unknown. However, some efforts have been made to offer a clear idea regarding the applications of nanomaterials in consumer products and its presence in the world market.

Since the presence of nanomaterials in the market implies its release to the environment, this information has been taken for having a wider landscape of the nanomaterials presence in the environmental matrixes, such as soil and water. Vance et al. [23] reported that around 64% of carbonaceous nanomaterials are embedded in solid products, whereas products of all other compositions are suspended in liquid. Of the few bulk nanomaterials that are available for purchase by consumers, the largest group (42%) consist of metal oxide nanomaterials. Metal and metal oxides were also the largest compositions for surface-bound particles and those suspended in liquid products.

According to Chatterjee [105], there are eight categories where the nanomaterials are majorly used, in increasing order: goods for children, appliances, automotive, cross-cutting, food and beverage, electronics and computers, home and garden, and health and fitness. Some examples are given as follows: TiO_2 and Ag nanoparticles are used to confer antimicrobial protection [22, 106], and TiO_2 and SiO_2 are used to provide protective coatings and for environmental treatments [107]. Cosmetic products contain silver, titanium, and gold nanoparticles [97] and nano-organic compounds.

A geographical inventory was reported by Chatterjee [105], where the number of products was registered by region, placing the United States of America as the first producer of 247 products, followed by East Asia (China, Taiwan, Korea and Japan) with 123 products. Also, Europe (U.K., France, Germany, Finland, Switzerland, Italy, and Sweden) with 76 products and others (Australia, Canada, Mexico, Israel, New Zealand, Malaysia, Thailand, and Singapore) with 27 products. This distribution is directly linked to the laws and regulations for each country or region [108].

Some other partial and complete inventories were done by Maynard et al. [109], Kannan et al. [110], and Berube et al. [111]. It is clear that this is useful for policy makers focused on the regulatory terms of consumers and producers of these products. Additionally, it is also important for having a clear idea about where and how nanomaterials are present in the environment after being used by consumers, allowing us to know and understand the routes by NM and NP arrived at the environment. The subsequent step would be to use tools such as life cycle analysis (LCA) to evaluate its impact on the environment [34, 112, 113].

Nanotechnologies to Remediate Soils

Nanotechnology is a virtually new environmental technology, and when applied to contamination problems it is known as nanoremediation [114]. This has recently been used for the treatment of hazardous waste sites. Lately, the use of nanotechnologies for environmental remediation has received significant attention from the scientific community [115], specifically in use for environmental remediation [24, 25, 115], in spite of that is recent technology field.

In 1996, Gillham was the first investigator who presented the idea of utilizing zero valent iron in permeable barriers reactive, based on their experience with the use of nanomaterials in decontamination with water-halogenated pollutants [116]. Some authors have synthesized nanoparticle zero-valent iron from chemical synthesis, while others from various extracts of green leaves, the same as those used for treating contaminants in aqueous solutions. In many cases the use of nanoparticles were effective to degrade contaminants such as organic halogenated hydrocarbons [117, 118], nitrates, heavy metals [119-121], insecticides, and dyes [122, 123].

There are very few studies that apply nanoparticles technology for the remediation of contaminants in soil, the research in this field has been used more for the decontamination of water or aqueous solutions [124]; according to the literature, the nanoparticles have the ability to adsorb and facilitate degradation of pollutants through various mechanisms such as redox reactions, surface processes, adsorption, ion exchange, surface complexation, and electrostatic interaction [125].

Shi et al. [124] tested nanoparticles zero-valent iron (nZVI), and iron nanoparticles zero valence on a matrix of bentonite (B-nZVI), in the removal of Cr (VI) in water and soil solution contaminated with this metal. As a result, they found that nZVI nanoparticles became more effective when the bentonite was introduced (B-nZVI) as carrier material due to the reduced aggregation and increased specific surface area; besides, they obtained a high rate of removal of Cr (VI), which increased directly proportional to temperature, and the amount of B-nZVI, but decreased as the pH increased [124-126]. In this project the use of nanoparticles B-nZVI for removal of Cr (VI), had great utility due to having a high surface area that is associated with its high reactivity, allowing it to work like an excellent agent capable of transforming, and degrade contaminants that use nanoparticles B-nZVI for removing Cr (VI) [124]. Likewise, the removal of other pollutants such as chlorinated organic compounds, pesticides, phenols, amines, and organic acids through such nanoparticles has been studied [126].

Other studies on this subject have shown that polybrominated diphenyl ethers, which are a class of environmental contaminants that can easily accumulate in the soil, can be degraded with zero valent iron nanoparticles immobilized in silica microspheres [127, 128]. The evaluation of the degradation decabromodiphenyl ether, from an aqueous solution with tetrahydrofuran (THF), was analyzed by Qiu et al. [127] and found that it was effective in a solution of THF/water to temperature and environmental pressure. Moreover, Xie et al. [128] evaluated this degradative ability to remove soil decabromodiphenyl ether, obtaining results that revealed that the removal efficiency or the performance of elimination of the ether of decabromodiphenyl was 78%. It was higher than the biomass of untreated plants with nanoparticles [128].

In other experiments, the growth of cabbage mustard in the presence of Cr (VI) and using iron nanoparticles supported on bio-carbon was evaluated; here the phytotoxicity of Cr (VI) was analyzed, and they found that the growth of cabbage mustard increased by treatment with nanoparticles, and also effectively reduced Cr (VI). Remediation tests Cr (VI) and total chromium (Cr) showed that immobilization efficiency was 100% and 91.94%, respectively, by applying 8 g per kg of soil [129].

Also, SiO_2 nanoparticles coated with a lipid derivative of choline have been used in the bioremediation of polycyclic aromatic hydrocarbons (PAHs) [130]; also, these nanoparticles were used coated with a lipid derivative of choline in the bioremediation of PAHs. Other nanomaterials that have been used are iron sulfide stabilized with carboxymethylcellulose; similarly, they were tested for immobilizing Hg in soils highly polluted with this metal [130].

Trujillo and Reyes [125] described the efficiency of zero valent iron nanoparticle to the remediation of contaminated aqueous solutions with ibuprofen in soils; being able to degrade ibuprofen in 54-66% of the initial amount in aqueous solutions and they obtained similar remediation efficiencies in the sandy soils. Olson et al. [131] conducted studies on soil with nanoparticle bivalent metals (Fe and Mg) to reduce the concentration of polychlorinated biphenyls (PCB) in soils achieving a reduction of 56% of the average concentration of PCBs, with a rate of average degradation of 19 mg kg^{-1} $week^{-1}$ [131]. Also, phytotoxicity tests conducted on samples of treated soil indicated almost complete restoration of PCB, evaluated based on high levels of germination; the same type of emulsified zero-valent iron was used in in situ treatment of polychlorinated soils, where there was the destruction of 2-clorobifenilo [131].

Other authors have emphasized the need to develop investigations on the ecotoxicity of the soil remedied with the use of nanotechnology [132], especially considering the tests with the use of plants that may be useful as sensitive indicators of soil toxicity [131, 132]. Also, the processes of nanoparticle degradation in the soil and its phytotoxicity need to be researched more, especially taking into account testing with the use of plants that may be useful as sensitive indicators of soil toxicity [133].

Recent research in 2016 refers to the toxicity of some nanomaterials and their effectiveness to interact in soil. For example, Fan et al. [134] studied the mechanism by which nano-TiO_2 affects the toxicity of Cu on Daphnia magna, mentioning that nanoparticles of titanium dioxide (TiO_2) can affect the toxicity of other pollutants and that the presence of organic matter can influence their combined toxicity. This study also found that the effect of nano-TiO_2 on the toxicity of Cu to D. magna decreased significantly with the presence of acid humic, which implies that the presence of organic matter in soil could decrease the remedial effect of such nanoparticles in the presence of some contaminants in soil. They mentioned that the effect of TiO_2 nanotoxicity of heavy metals depends on the adsorption capacity of heavy metals in the nano-TiO_2; and absorption and stability in the formation of complex metal-nano-TiO_2 and the presence of dissolved humic acids, which affect the ability of nano-TiO_2 to accumulate Cu [134].

Although many types of nanoparticles can be used for soil decontamination, almost all researchers only consider the use of nanoparticles of zero-valent iron for practical field application; it is also interesting to note that most studies refer to decontaminating primarily saturated soils. Only a few studies have addressed the remediation of contaminated – not saturated – soils [135]. The different existing publications in 2016 refer to different experimental parameters and of synthesis of nanoparticles, which makes it difficult to make a comparison between the efficiencies of different used nanomaterials, since they vary in their structure, composition, and morphology, and all this affects adsorptive capacity opposite to similar contaminants, and knowledge of their ability to degrade different types of pollutants is still scarce.

Analysis of the literature highlights the need for more studies on nanomaterials, given the lack of information on the mechanisms of regeneration and reuse, and its large-scale application and effectiveness in treating industrial wastewater real and contaminated soils; nevertheless, existing results to date indicate that this remediation technology represents a good alternative to traditional technologies. Nowadays, little is known about the mechanisms of nanomaterials on the ground, their life cycle, the release of metal ions, and their impacts on different ecosystems. Nanoremediation has different advantages, such as reducing the cost, cleanup time of contaminated sites, and they can be used on a large scale. But it is necessary to make deep studies evaluating the effect of nanoremediation on the ecosystem level in order to prevent any adverse environmental impact.

Effect of Anthropogenic Nanosized Materials on Soil Environment and in the Environment

Why Nanotechnologies?

From the definition of nanotechnology, it is possible to observe the many benefits that this technique can bring to sciences. This technology has been reported to be beneficial in medicine [136-140], physics [136, 141], genetics [142-144], and, most recently, in environmental sciences, among many other areas [123, 145-147]. We must highlight the fact that nanotechnologies have been reported as reliable [148], feasible [140], promising [149], practical [150], precise [151], cheap and effective [152], emerging [153], powerful [154], and economically feasible [155].

Nanotechnology Examples in Environmental Sciences, Specifically for Soil Remediation

Nanotechnology in environmental sciences is still new, and many of the results of the research in this field are still in the process of being marketable in the form of nanoproducts. It was not established with certain clarity what was exactly a nanoproduct in the environmental area. Nevertheless, Cinelli et al. [156] established the criteria for evaluating the sustainability of nano products. The authors identified six main areas of environmental nanoproducts, including environmental impacts. Thus, we should include nanotechnologies for soil remediation under the already cited category. Examples of the use of nanoproducts in environmental sciences are: i) the ones reported by Ali et al. [157], for the applications on photocatalytic degradation of organic pollutants; ii) the study of Li et al. [158] in the area of propulsion; iii) studies of Scognamiglio et al. [159] in biosensor technology for endocrine-disrupting chemicals; iv) studies by Elango and Roopan [160] for the degradation of methylene blue, an important water pollutant; and v) studies by Begum et al. [161] for the quick sensing of environmental stimuli (as pH, ion strength, biological molecules). More studies in nano molecules for sustainability procedures are the ones from Li et al. [162] for the construction of hydrogels for bioanalysis purposes, and the studies of Kannan et al. [110] describing the use of hydrothermal carbonization materials that convert wet biomass into a cool-like material with applications in the field of energy. Additionally, studies by Pereira et al. [163] on the use of microorganisms during the biosynthesis of metallic nanoparticles and studies by Bogdan et al. [164] reporting the creation of nanomaterials with self-disinfecting and self-cleaning surfaces, have been described in the literature. It has to be noted that many of them are in experimental phases and cannot be found in the market.

More recent studies show some applications of this nanotechnology in the area of agriculture. Peters et al. [165] report the in-development applications of nano-encapsulates and nanocomposites for food and feed additives, biocides, pesticides, and food contact materials. Also, Ibrahim et al. [166] report the application of nanomaterial as amendment agents for phytoremediation purposes and the use of stabilizers to enhance their performance. Nathanail et al. [29] indicated the existence of the NanoRem European Research project, which finances studies directed to develop the appropriate nanotechnology for contaminated soil remediation. They report the injection of nanoparticles into contaminated groundwater to result in a minimal level of risk because of the peculiar pathway these particles unleash while unfolding the contaminant macromolecules. Das et al. [145] reports the increasing use of diverse materials in their nano form (iron, titanium, dioxide, silica, zinc oxide, carbon nanotubes, dendrimers, polymers, etc.) to decontaminate soils.

A comprehensive review from Dadrasnia et al. [167] exposed the remediation options available in the case of oil/spill contamination with the emphasis on biological treatments via advances in nanotechnology (supplement addition and phytoremediation). In the area of simulation, Wang et al. [139] reported the use of the proposed coarse-grained molecular dynamics simulation, useful for studying the water/oil/solid systems, which could be of a broader use in industrial applications, including environmental sciences. This proposed model is expected to promote the development of this type of simulation to study multiphase systems. Interesting is the report from Husen and Siddiqi [168] describing the use of plants or their extracts, providing a biological system route for the generation of several metallic nanoparticles. This last represents a more eco-friendly route for the production of these useful nanoparticles. The so-called photosynthesis represents a viable route for the production of metal and metal oxide nanoparticles, allowing a controlled synthesis with well-defined size and shape, with broad application in industry, including soil bioremediation.

More specifically, nanotechnology in soil remediation and bioremediation has been recently introduced as a worthy technology in the last decade. The study by Nguyen et al. [75] generated a new strain of the genus Cronobacter, which have been studied for their capacity to remove selenite with 100% efficiency by taking up electrons from an electrode that performs selenite reduction. The use of produced nanoparticles by microbial selenite reduction may represent an alternative for industrial recovery purposes. An extensive investigation from Fernandez-Llamosas et al. [169] report the isolation of Azoarcus bacterial genus as a physiologically versatile group of beta proteobacteria. It is defined as a facultative anaerobe genus combining the ability to anaerobically and aerobically biodegrade a wide range of aromatic compounds, including toxic hydrocarbons (toluene and m-xylene) while and endophytic lifestyle in the root of rice. Authors conclude the technique to be suitable for more sustainable agricultural practices in bioremediation strategies.

Pollmann et al. [170] reported the so-called biohydrometallurgical processes, which include the operations of biomining, bioleaching, and bio-oxidation, facilitating the degradation of minerals. Other interesting processes are bioaccumulation, bioflotation, bioprecipitation, and biomineralization, which are processes that have been very well studied but with recent practical applications because of the rapid development of novel techniques as nanoscience technologies. The mentioned processes are thought to be an environmentally friendly and efficient alternative for industrial applications, including contaminated soil bioremediation.

Interesting is the concept of bioprospecting, introduced by Beattie et al. [171]. Benefits of this technique include unrespecting products useful for industry, chemicals, metabolic pathways, structures, and materials. To 'bioprospect' a remediation technique for soil remediation would involve the decrypting of the involved pathway in the mineralization of soil pollutants, which can be strongly benefited by the support of nanotechnologies. Emtiazi et al. [172] reported the use of nanofilters and nanofilters plus a microbe to be 45 and 91% more efficient, respectively, for the removal of Methyl ter-butyl eter, used in gasoline and polluting soils. Bozarth et al. [173] have reported a source of nanotechnological procedures for bioremediation of contaminated soils, which includes the diatom molecular biology as well as the culturing conditions and photobioreactor efficiency. The future in soil bioremediation with the use of nanotechnologies is the one represented by experiments from Juwarkar et al. [174], reporting cell isolates of Bacillus sphaericus (named JC-A12) from a uranium mining waste pile. The isolates can accumulate toxic metals (U, Cu, Pb, Al, Cd) as well as precious metals (U, Cu, Pd(II), Pt(II), Au(III)). The special capabilities of the cells are highly interesting for the cleanup of uranium-contaminated wastewaters and soils. An extensive overview of nanotechnology-supporting and -improving bioremediation procedures is presented by Juwarkar et al. [174]. Successful case studies from this last include bioremediation studies in vadose soils, bioremediation of contaminants from mining sites, air spraying, slurry phase bioremediation, and phytoremediation from pollutants and heavy metals, as well as vermicomposting.

So, are Nanotechnologies a Sustainable Procedure for Soil Remediation?

A commonly accepted definition of sustainability is "the ability to pursue an economic prosperity maintained over time while protecting the global natural systems and providing a high quality of life for people" [175]. From the results of the research of all the cited authors in this review, we want to propose an affirmative answer to the original question, but the answer has several edges, i.e., social, environmental, and economic concerns regarding nanoremediation have to be attended in order to improve the technologies, decreasing costs and shaping a sustainable future. Procedures and researchers cited in this review claim that the results are useful for the production of commercial applications (economic prosperity) and also claim that the procedures are "environmentally friendly" to protect natural systems worldwide.

It should not be forgotten that all natural systems are self-regulated but, in most cases, the pollution's concentration is far above the environment's natural ability to decontaminate by itself, i.e., natural attenuation is not always possible. In addition, to our best knowledge, there is no evidence regarding the natural attenuation of nanopollutants.

Our activities, and we as humans, have changed the global natural balance. Then, nature and wisdom are providing us with tools to face up to pollution and degradation through nanotechnology. All we have to do is to understand the system where we are working – especially in the area of soil remediation. If we create more eco-friendly technologies for agricultural procedures, improve industrial processes, increase the regulatory framework, and educate the society, remediation techniques would not be necessary ever again. It has to be remembered that 1 cm^3 of soil has more than 3000 species of microorganisms and more than 1×10^7 organism cells. Soil organisms are very important for environmental balance and one of the key issues for shaping a sustainable future is the preservation of biodiversity for maintaining the global natural balance. Until now, there is no information regarding the effect of nanotechnologies on global biodiversity, but there are several attempts to put the nanoscience and the nanotechnology as some of the best humanity advances in recent years. Will some nanotechnologies be our pitfall by ourselves?

How do Patents Increase the Use of Anthropogenic Nanosized Materials in Environmental Remediation?

Who is Patenting New Nanotechnologies to Improve Environmental Quality?

According to the Derwent Innovations Index from Web of Science (by restricting the search field topic

Table 1. Authors, institutions, or people to whom patents were assigned, plus patent numbers and reference.

Author; Institution	Patent numbers; Reference
Zhang, C.; Yantai Inst Coastal Zone Res Sustainable	CN106475052-A; [176] CN105950155-A; [177] CN105950180-A; [178] CN105950181-A; [179]
Yang, Z.; Univ. Cent. South	CN105733593-A; [180] CN105733588-A; [181] CN105647539-A; [182] CN105598158-A; [183]
Li, J.; Liu, X.	CN104801540-A; [184] CN104807762-A; [185] CN104801534-A; [186]
Cheng, G.; Jiangsu Gaiya Environmental Eng. Co. LTD.	CN105505397-A; [187] CN105505398-A; [188] CN105441082-A; [189[
Fang, Z.; Univ South China Normal	CN105131960-A; [190] CN105013811-A; [191] CN103157810-A; [192]
Feng, X.; Gefeng Environmental Protection Technolo	CN106430598-A; [193] CN206051687-U; [194]
Bezbaruah, A.; Ndsu Res Found.	WO2014168728-A1; [195] WO2013173734-A1; [196]
Chen, M.; Inst Mineral Resource Chinese Acad Geolo	CN104893732-A; [197] CN104129841-A; [198]

to 'nano*' and 'remed*'), during the last five years 154 patents have been assigned regarding the topic of nanoscience, nanotechnology, and remediation. After that, we did a manual analysis to set the relevant patents that met the established search topic.

During the last five years only eight authors have published two patents or more regarding nanotechnology, nanoscience, and remediation of soil or water (Table 1).

Main Benefits of Patents Regarding the New Nanotechnologies to Improve Environmental Quality

In recent years, scientists and technologists have gone further to create new devices or tools in order to improve environmental and human health. Some patents improved other technologies throughout the synthesis of new nanomaterials in order to remediate the environment and save energy [176]. Additionally, we have built a soil-conditioning agent for remediating soil contaminated by heavy metal and reuse the conditioning agent at low cost [177]. Another patent argues that lime powder, hydroxyapatite, nano-silica, gravel, activated carbon, and calcium peroxide can permanently remove heavy metals in the soil, and reduce the toxicity and the leaching concentration of heavy metals in soils by a straightforward and rapid industrial process [178]. Nanocomposites of attapulgite are a repairing agent used in ecological restoration projects in mining areas, and soil remediation projects in agricultural land polluted with heavy metals. These nanocomposites have a particular advantage that quickly and efficiently stabilizes the soil, while they are environmentally friendly [179].

Some bioremediation techniques have also seen patents in order to restore heavy metal- polluted soils. Chai et al. [180] patented a microbial assembly synthesis method for preparing an arsenic-contaminated soil remediation fixing agent. The method enables the preparation of an arsenic-contaminated soil remediation fixing agent with an environmentally friendly process. It does not produce secondary pollution, does not disrupt the physical and chemical properties of the soil, and is non-toxic [181]. Additionally, a method for preparing phosphorus-based bio-carbon material for remediating cadmium-contaminated soil utilizing culture medium of filamentous fungus was also patented [182, 183].

In addition, a remediation method of a contaminated site involves the coating surface of zero-valent nano iron with organic polymer layer. This technology injects the coated zero-valent nano iron into contaminated soil through an injection well, oxidizing zero-valent nano iron and injecting reducing bacterium solution into the contaminated soil, while the growth of indigenous microorganisms and the degradation of pollutants are accelerated [184, 185]. A similar patent was assigned in which a method for degrading organic pollutants of persulfate in water is described [177]. This method enables a high remediation rate of organically polluted water, with strong free-base oxidation ability and a stable reaction system at wide pH range.

A new technology to remove a contaminant from an aqueous medium required bare nanoscale zero-valent iron (NZVI) particles or calcium (Ca)-alginate entrapped NZVI under conditions and for a time effective to sorb the contaminant [195]. According to the inventor, phosphate, selenium, and other collected nutrients can be recycled as an agricultural fertilizer. The method is a green technology that follows the principles of reduce, reuse, and recycle [195]. Additionally, a new functionalized amphiphilic plant-based copolymer was patented. It was stated that the copolymer facilitates improved dispersion and suspension of iron nanoparticles (FeNPs) in water for application in groundwater remediation [196]. Furthermore, the copolymers are surface active due to their amphiphilic nature. Thus, the compounds may provide an additional advantage, i.e., antimicrobial activity.

Another patent has described the synthesis of a magnetic nanomaterial with a core made of a magnetic material while an organic matter cladding layer is provided outside the core. This magnetic nanomaterial is used to remediate heavy metal-contaminated soil [186].

A method for preparing iron-based bio-char material used for remediation of arsenic-polluted soil was also patented [181]. The method enables preparation of iron-based bio-char material with a simple process and at low cost [181].

Some mixtures of nanomaterials have also been patented. For example, a mixture of nano-material containing bentonite, fly ash, magnesium nitrate, barium oxide nanoparticles, polymeric ferric aluminum silicate, stachydrine, dimethylol urea calcium aluminate, magnesium aluminosilicate, and phospholipid was patented in 2015 in order to remediate soils polluted with lead or copper ion [187-189]. Another mixture was patented as a remediating agent for heavy metal lead-cadmium and lead-cadmium sulfide composite-contaminated soil [197]. This remediating agent contains 5-20 parts mass modified carbon nanotubes, 10-60 parts mass modified clay mineral, and 10-75 parts mass lime. According to the inventors, the remediating agent can be prepared in a simple and economical manner, and reduces 75-90% cadmium [197].

The preparation of composite material used for in-situ remediation of lead-contaminated soil has also been patented [190]. According to the authors, the method provides soil-remediation composite material having high soil repairing efficiency. Additionally, the same authors patented a method for preparing biochar particles used in preparing load-type zero-value nano-iron particles for in-situ remediation of chromium-contaminated soil [191]. Additionally, a method for preparing dispersed nanometer nickel/iron bimetallic particles that are utilized for in-situ remediation of poly brominated diphenyl ethers was also patented [192].

In addition to the nanomaterials, other devices also have been patented in order to remediate soil or water. An ecological bag filled with multifunctional nanocomposite material was patented to remove heavy metals, total nitrogen, and phosphorus from soil or water [193, 194]. However, this device cannot be found in the market yet.

In general, the patents described above represent a sustainable practice that facilitates efficient recovery of heavy metals or wasted nutrients, and the dissipation of pollutants (at least this is the genuine intention of the inventors). The inventors argue that these technologies are well suited to the needs of the fertilizer industry, municipalities, and pollution control agencies. In this way, for example, when used as fertilizer, NZVI or Ca-alginate-entrapped NZVI supply not only the adsorbed nutrient (e.g., phosphate or selenium), but also iron. In addition, the release of nutrients (e.g., phosphate, selenium, and iron) takes place over time, thus providing a time-release action. Therefore, if everything goes according to the inventors' plans, the nutrients are supplied in a bioavailable form and can be efficiently taken up by plants and microorganisms during the vegetative or reproductive growth.

Several patents have been reported arguing for the environmentally friendly synthesis of new nanomaterials with specific and worthy properties in order to dissipate pollutants and/or remediate contaminated sites. However, additional research regarding the ecological effect of using these modern nanomaterials for several years has to be done. Otherwise, these patents might jeopardize the sustainability which is widely sought by scientists, technologists, politicians, and common people worldwide.

Conclusions

Nanotechnologies and nanosciences have been very useful for delivering some materials, products, or services with better characteristics compared to their respective bulk material. Also, these areas have also provided some nanosized materials to the environment, and the human and environmental concerns have been raised. However, nanotechnologies have also been used to dissipate soil pollution, but benefits and risks have been discussed recently. It is well known that some strategies to remediate polluted soils through nanotechnology might be accomplished, but some questions have to be answered prior the spread of nanoremediation, i.e., nanoparticle toxicity has to be assessed while the standardization of techniques should be set by scientists and decision-makers worldwide. The cutting-edge knowledge regarding the use of nanoparticles to decontaminate soils has to move forward, but environmental quality, human health, and social welfare should also be ensured. Otherwise, these patents regarding modern nanomaterials might jeopardize sustainability.

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Conflict of Interest

The authors declare no conflict of interest.

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10.2.2 Review. Nanotoxicidad: retos y oportunidades

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Nanotoxicidad: retos y oportunidades

Nanotoxicity: Challenges and opportunities

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RESUMEN: La nanotoxicología es un campo emergente que evalúa los peligros y riesgos humanos o medioambientales causados por estructuras de menos de 100 nanómetros. El objetivo es documentar y discutir algunos aspectos sobre la toxicidad de materiales de dimensiones nanométricas en el ser humano, el medio ambiente y el sector agrícola. Los resultados indican la existencia de suficientes artículos científicos que documentan la toxicidad de esos materiales. Sin embargo, también se presenta una serie de ventajas y usos potenciales que en el corto tiempo podrá disfrutar el ser humano, siempre y cuando se tomen algunas consideraciones relevantes que fortalecerán las competencias de los científicos o tecnólogos jóvenes. Continuar con la formación de recursos humanos y el desarrollo científico y tecnológico de estructuras nanométricas es necesario, pero, se debe tener cuidado de no cometer errores históricos como aquellos en los que productos 'evaluados científicamente' como el DDT o el asbesto tuvieron que ser retirados del mercado por sus efectos secundarios, tóxicos o carcinogénicos.

PALABRAS CLAVE: bienestar social, contaminación, desarrollo sustentable, medio ambiente nanopartícula, patente, salud pública.

ABSTRACT: Nanotoxicology is an emerging field that assesses human and environmental hazards and risks caused by structures of less than 100 nanometers. The objective is to document and discuss some aspects of the toxicity of materials of nanometric dimensions in humans, the environment, and the agricultural sector. The results indicate that there are enough scientific articles documenting the toxicity of these materials. However, there are also advantages and potential uses that humans can enjoy in the short time, provided that some relevant considerations are taken that will strengthen the skills of young scientists or technologists. Human resources training and scientific and technological development of nanometric structures should be continued. However, care should be taken in order to not commit historical errors such as those where products were 'scientifically proven' like DDT or asbestos which, some years later, had to be removed from the market for its toxicity, carcinogenicity or its side effects.

KEYWORDS: social welfare, contamination, sustainable development, environment, nanoparticle, patent, public health.

Introducción

Durante los últimos años la nanociencia y la nanotecnología han contribuido con conocimiento y desarrollos tecnológicos que muy pocos imaginaron

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algunas décadas atrás. Sin embargo, hoy en día prácticamente cualquier dispositivo electrónico tiene al menos un componente de dimensiones nanométricas, mientras que con mayor frecuencia se comercializan materiales de construcción, cosméticos, ropa y empaques que también contienen nanomateriales. Sorprendentemente, también hoy se pueden adquirir productos que deben cumplir con estrictas regulaciones sanitarias, como medicamentos y alimentos, los cuales tienen componentes tecnológicos producto de la nanociencia y la nanotecnología.

En la actualidad, casi 2 mil productos que contienen partículas, materiales o dispositivos de dimensiones nanométricas se están comercializando alrededor del mundo debido a sus novedosas propiedades físicas, químicas o biológicas, lo cual le da al producto terminado propiedades o características muy específicas y apreciadas (León–Silva *et al*., 2016). Sin embargo, cuando los productos con componentes de dimensiones nano concluyen su vida útil y son desechados inadecuadamente, podrían convertirse en un problema de contaminación ambiental o de salud pública (León–Silva *et al*., 2016; Valerio–Rodríguez *et al*., 2016). Así, se estima que más de 110 mil toneladas de materiales de dimensiones nano podrían ser eventualmente liberadas al suelo, agua o aire y más de 260 mil toneladas podrían ser dispuestas en rellenos sanitarios, aun cuando no se cuenta con tecnologías apropiadas para su disposición final (Keller *et al*., 2013).

Al día de hoy, la población mundial es de más de 7,600 millones de seres humanos y se estima que para el año 2050 se alcanzarán los 9,800 millones. Lo anterior representa una creciente demanda de agua, energía y alimentos, y una presión sobre los científicos, tecnólogos, sociólogos y economistas para proveer suficientes servicios y bienes de calidad, a precios asequibles. Además, los científicos, tecnólogos y tomadores de decisiones deben hacer frente a la creciente contaminación de suelo, agua y aire, que sólo en 2016 cobró la vida de más de 9 millones de personas en todo el mundo, con un costo de más de 4.6 billones de dólares (Das y Horton, 2017).

Durante el año 2016, más de 815 millones de personas padecieron hambre en todo el mundo, de acuerdo con la Organización Mundial para la Alimentación y la Agricultura (FAO, 2017), por lo cual es imprescindible que el sector primario crezca notablemente, en particular la agricultura, la ganadería, la apicultura, la acuicultura y la silvicultura. La agricultura debe incrementar la producción de alimentos inocuos y de alta calidad, a pesar de las limitaciones relacionadas con la escasez y contaminación de suelo y agua. Recientemente, la nanotecnología ha producido y empleado diversos materiales en el sector agrícola, especialmente diseñados para hacer frente a los problemas de este sector. Nanofertilizantes, nanopesticidas, nanocápsulas, nanopelículas, nanosensores y nanotransportadores se han evaluado en diferentes cultivos para una gran variedad de usos como: i) liberación controlada de nutrientes; ii) inhibición de microrganismos patógenos; iii) control de enfermedades; iv) transporte de fertilizantes; v) reguladores de crecimiento vegeta;, vi) detección de microrganismos benéficos, y, vii) incremento de vida postcosecha, etcétera (Fernández–Luqueño *et al.*, 2016).

Sin embargo, después de que esos desarrollos tecnológicos de dimensiones nanométricas realizan su función y completan su ciclo de vida, quedan dispersos en el medio ambiente. No obstante, esos materiales nanométricos desarrollados para impulsar el sector agrícola no son la única fuente de nanomateriales en los campos agrícolas, debido a que como se indicó anteriormente, miles de toneladas de nanomateriales llegan a los suelos agrícolas a través de la deposición atmosférica, el riego con aguas residuales, el uso de biosólidos como fertilizantes agrícolas, o bien a través de la inadecuada disposición final de residuos y basuras.

El objetivo de esta investigación es discutir el efecto tóxico de nanopartículas metálicas en seres humanos, el medio ambiente y en el sector agrícola, y presentar algunos criterios que podrían ser útiles durante los procesos de síntesis, uso y disposición final de materiales con dimensiones nanométricas.

Materiales y métodos

Esta investigación toma como base la definición de nanotoxicología descrita por Dusinka *et al.* (2017), donde se indica que la nanotoxicología es un campo emergente encargado de la evaluación de peligros y riesgos humanos y medioambientales causados por estructuras de menos de 100 nanómetros (nm). En este sentido y bajo la consideración de que las plantas cultivadas son un componente del medio ambiente es como los autores realizaron un estudio bibliográfico en el cual describen evidencias del efecto de las estructuras de menos de 100 nm sobre los seres humanos, el medio ambiente y el sector primario, en particular sobre la agricultura. Las evidencias reportadas aquí provienen de publicaciones de diversos grupos de investigación de diferentes partes del mundo, las cuales se contrastan y comparan con resultados publicados por el grupo de investigación al que están adscritos los autores del presente documento.

De la síntesis de la estructura nanométrica al producto, patente y bien comercializable

En este momento es posible encontrar miles de artículos científicos en los que se describe el proceso de síntesis y caracterización de nuevos materiales de dimensiones nanométricas pero, salvo algunas excepciones, esas investigaciones carecen de estudios sobre toxicidad, impacto ambiental y uso potencial. Sólo en los años 2015, 2016 y 2017 se publicaron más de 315 mil artículos científicos, con el prefijo 'nano' en el título, en diversas revistas internacionales incluidas las de la prestigiosa base de datos Web of Science™. Sin embargo, sólo en menos de 3 mil de esos artículos científicos se hace referencia al medio ambiente, ya sea para explicar su impacto a éste o bien, para resaltar aplicaciones 'potenciales' relacionadas con él.

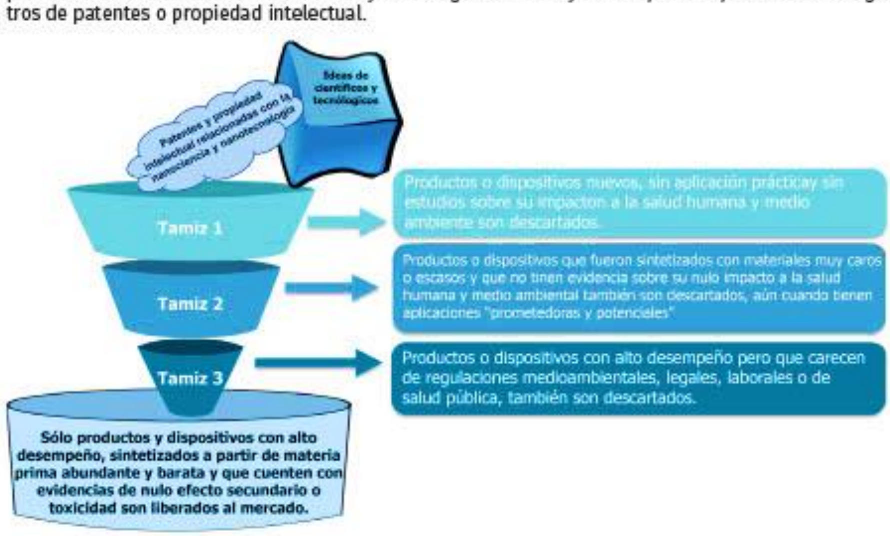
11(20), 7-16, enero–junio 2018 | http://dx.doi.org/10.22201/ceiich.24485691e.2018.20.64105

En este sentido, proponemos una serie de tamices (figura 1), en los que claramente algunos productos de dimensiones nanométricas quedarían sin posibilidades para competir en un mercado de productos terminados, debido a que carecen de uso potencial y de estudios relacionados con el impacto ambiental y toxicidad, aun cuando hayan sido diseñados y sintetizados bajo cuidadosos y estrictos estándares académico–científicos.

Cambio de paradigma

Sin duda, el diseño de nuevos materiales, su síntesis y su caracterización son actividades complejas que en la mayoría de los casos requieren un bagaje amplio de conocimientos, un dominio de diversas técnicas de laboratorio y un manejo de sofisticados y costosos equipos de laboratorio. Además, es común que los grupos transdisciplinarios dedicados a estas actividades sean los que dominen ciertas áreas del conocimiento y por tanto, tengan el liderazgo nacional o internacional sobre la síntesis y caracterización de materiales muy particulares. En este sentido, como lo describen León–Silva *et al.* (2016), los grupos de investigadores tienen dominado el proceso de síntesis de materiales nanométricos, sus aplicaciones, sus rutas de exposición (en algunos casos) y los factores de toxicidad (en casos excepcionales), pero no han trascendido al cambio de paradigma en el que se consideren aspectos como las 17 metas del desarrollo sustentable o las 5R (Repara, reduce, reutiliza, recicla y recupera; figura 2).

FIGURA 1. Serie de tamices en los que se resaltan algunos criterios por los que ciertos productos con dimensiones nanométricas podrían quedar fuera del mercado de productos terminados, aun cuando partan de una idea con bases científicas y tecnológicas sólidas y cuando, incluso, cuenten con registros de patentes o propiedad intelectual.



Fuente: Elaboración de los autores.

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FIGURA 2. 5R para la síntesis y uso de materiales a escala nanométrica.

Fuente: Elaboración de los autores.

Evidencias de nanotoxicidad

En esta sección se presenta una breve descripción de evidencias de nanotoxicidad. Por su relevancia, se indican únicamente los resultados publicados en revistas científicas de alto impacto que se encuentran dentro del primer cuartil de las áreas de toxicología, ciencias medioambientales o, ciencia y tecnología de alimentos. Además, esta sección se divide en tres subsecciones: i) nanotoxicidad en seres humanos; ii) nanotoxicidad en el medio ambiente, y, iii) nanotoxicidad en el sector agrícola.

i) Nanotoxicidad en seres humanos

La nanotecnología médica tiene amplia relevancia, considerando el uso terapéutico potencial y real (actual) de algunos materiales de dimensiones nanométricas. Más aun, la nanociencia y la nanotecnología han tenido contribuciones sobresalientes en el diseño y fabricación de equipos médicos. No obstante, se han descrito algunos efectos tóxicos en el cuerpo humano (tabla 1).

ii) nanotoxicidad en el medio ambiente

Todos los materiales de escala nanométrica llegan al medio ambiente en corto o largo plazo. Eso implica que el medio ambiente siempre será el destino final de los nanomateriales y por tanto se acumularán en él; al respecto, se han hechos estudios sobre toxicidad de nanomateriales en cuerpos de agua, organismo del suelo, entre otros (tabla 2).

11(20), 7-16, enero–junio 2018 | http://dx.doi.org/10.22201/ceiich.24485691e.2018.20.64105

TABLA 1. Principales efecto tóxico de nanomateriales sobre los seres humanos.

Breve descripción de la evidencia	Referencias
Los autores sostienen que con la rápida expansión de la nanomedicina, el conocimiento relacionado con el comportamiento de nanopartículas en el interior del cuerpo ha escalado rápidamente, por lo que la nanotecnología biomédica deberá enfocarse en las interacciones de las nanopartículas con el sistema inmune por razones de seguridad y eficacia.	Neagu *et al.*, 2017.
Los autores reportan que las nanopartículas pueden entrar a las células humanas por diversas vías e inducir citotoxicidad, genotoxicidad, producción anormal de especies de oxígeno reactivo, activación endotelial, inflamación y disfunción de orgánulos.	Cao *et al.*, 2017.
Los investigadores sugieren que la acumulación de nanopartículas de TiO_2 durante varios años podría dañar el hígado u otros órganos del cuerpo humano.	Bello y Warheit, 2017.

Fuente: Elaboración de los autores.

TABLA 2. Principales efectos de materiales de dimensiones nanométricas sobre el medio ambiente.

Breve descripción de la evidencia	Referencias
La acumulación, transformación, transporte y biodisponibilidad de nanopartículas metálicas en el ambiente es bien conocida, lo que implica su consumo por plantas, organismos o peces.	Amde *et al.*, 2017.
Las nanopartículas de Ag en suelo afectan a las lombrices de suelo (*Eisenia fetida*) debido a que se activan diferentes mecanismos que ocasionan la pérdida de peso y mortalidad.	García–Velasco *et al.*, 2016.
Las nanopartículas de TiO_2 en el suelo afectan significativamente las poblaciones de microrganismos nitrificantes.	Simonin *et al.*, 2016.

Fuente: Elaboración de los autores.

Es importante destacar que los materiales con dimensiones nanométricas también han presentado resultados prometedores para purificar agua o aire, reducir la concentración de CO_2 en el medio ambiente y para degradar o remover contaminantes de suelo, agua o aire. Incluso, se han diseñado nano–robots con 'movimiento propio' e 'independiente' para 'atrapar' la mayor cantidad de contaminantes del agua (Jurado–Sánchez *et al.*, 2015).

iii) Nanotoxicidad en el sector agrícola

A pesar de las evidencias publicadas en las que se documenta la toxicidad de nanomateriales en cultivos agrícolas (tabla 3), es importante señalar que algunos grupos de investigación están trabajando con la inducción de estrés a través de la adición de nanomateriales, con el fin de que la planta sintetice metabolitos de alto valor o bien, para que se acumulen ciertos iones en el fruto, con el objetivo de incrementar el aporte nutrimental de los frutos.

En general, se ha reportado que las estructuras de dimensiones nanométricas afectan significativamente los cultivos agrícolas en la germinación, emergencia, actividad fotosintética, producción de biomasa, componentes de

http://dx.doi.org/10.22201/ceiich.24485691e.2018.20.64105 | 11(20), 7,-16, enero–junio 2018

rendimiento y calidad del fruto. Además, a nivel molecular, también se ha determinado que los nanomateriales modifican la síntesis de diversos metabolitos relacionados con la producción de especias de oxígeno reactivo, genotoxicidad, alteración en membranas celulares, etc. (tabla 3).

Retos y oportunidades

Debido a que apenas en los últimos años la nanociencia y la nanotecnología han llamado la atención de especialistas de todas las áreas, aún es necesario estandarizar metodologías de síntesis y caracterización. Además, se requieren recursos económicos para la adquisición de equipos y también se necesita capacitación de recursos humanos porque hay diversos aspectos que requieren atención. Por ejemplo, es muy fácil caracterizar una nanopartícula 'X' pura o con alta pureza cuando ésta se encuentra en un vial, pero es prácticamente imposible caracterizar esa nanopartícula 'X' cuando ella está libre en el medio ambiente. Más complicado aún es determinar la concentración de esa nanopartícula 'X' cuando sólo la tenemos en el medio ambiente. Por lo anterior, el desarrollo de equipos y metodologías de identificación y caracterización siguen siendo una prioridad.

Adicionalmente, aún falta mucho por hacer en relación con la estandarización de pruebas de toxicidad de nanopartículas y con el uso de condiciones ambientales y organismos modelo en los que se podrían realizar las pruebas, con el objetivo de lograr reproducibilidad. Recordemos que uno de los grandes problemas ligados a las pruebas de toxicidad es la diversidad de datos en las publicaciones y la gran diferencia o variabilidad en sus conclusiones, las cuales suelen ser opuestas a las de sus pares. De tal modo, hoy en día es posible encontrar artículos científicos que reportan experimentos muy similares, con el mismo tipo de organismo y materiales nanométricos semejantes, pero podríamos agrupar estos artículos en aquellos que indican

TABLA 3. Principales efectos de nanomateriales sobre los cultivos agrícolas.

Breve descripción de la evidencia	Referencias
Se evaluaron nanopartículas de plata con y sin recubrimiento. En todos los casos, las raíces de cebolla activaron su mecanismo oxidativo y mostraron signos de toxicidad.	Cvjetko *et al.*, 2017.
Presenta una discusión de más de 170 referencias bibliográficas relacionadas con el efecto de nanopartículas metálicas sobre el crecimiento y fisiología de cultivos de importancia mundial. En general, indica que las nanopartículas alteran la nutrición mineral de los cultivos y su fotosíntesis, causan estrés oxidativo e inducen genotoxicidad.	Rizwan *et al.*, 2017.
Señala que los nanomateriales empleados en la agricultura podrían causar serios daños a los tejidos de las plantas y generar disfunciones en la membrana celular a través del estrés oxidativo.	Pradhan y Mailapalli, 2017.

Fuente: Elaboración de los autores.

efectos tóxicos, otros que apuntan efectos benéficos y otros que reportan efectos nulos.

Algo muy importante por hacer, es formar investigadores con visión holística y con un compromiso ambiental y social. Es claro que no es posible formar todólogos, ni se debe pretender formarlos; sin embargo, si es responsabilidad de los mentores 'sembrar inquietudes' en los estudiantes, de modo que no sólo se preocupen por sintetizar, caracterizar y publicar, sino también considerar como un deber concientizar a los estudiantes para que sea posible la formación de recursos humanos de alto nivel con liderazgo y responsabilidad social y ambiental. Lo anterior se ha considerado muy pocas veces y, créanlo, como sociedad nos está pesando.

¿Es posible obtener ventajas de la nanotoxicidad?

Efectivamente, algunos investigadores han reportado ventajas de la toxicidad de las nanopartículas. Por ejemplo, ahora es necesario controlar algunos patógenos a través del uso de nanopartículas, porque dichos organismos adquirieron resistencia contra antibióticos tradicionales. Otra ventaja de gran interés médico ha sido la toxicidad que tienen ciertas estructuras nanométricas, las cuales tienen toxicidad contra células con cáncer. Lo complicado de estas aplicaciones prometedoras es cómo identificar las dosis 'ideales' para únicamente obtener el beneficio sin correr riesgos o bien cómo identificar las nanoestructuras 'amigas' que bajo ninguna circunstancia nos causarán daño. Es claro que aún falta mucho por hacer, por lo que el apoyo de nuevos y mejores científicos o tecnólogos será necesario y, por supuesto, equipamiento de punta también será requerido.

Conclusiones

Los materiales con dimensiones nanométricas pueden ser diseñados y sintetizados con propiedades particulares, específicas e inigualables para obtener ventajas competitivas, comparados con materiales similares de dimensiones mayores. Sin embargo, es necesario considerar las implicaciones ambientales, sociales y económicas, e incluso tecnológicas, que podría tener su uso intensivo y extensivo, cuando las regulaciones son mínimas, por no decir nulas.

El efecto tóxico de algunas estructuras nanométricas ha sido ampliamente reportado. Sin embargo, también se han documentado los beneficios potenciales que tienen los materiales de dimensiones nanométricas cuando se aplican a los cultivos en dosis específicas. En este sentido, el efecto de los nanomateriales sobre los cultivos está en función del tipo de material, la dosis aplicada, la vía de administración, el tiempo de contacto nanomaterial-planta, la carga superficial, la etapa fenológica del cultivo, el tipo de cultivo y la presencia, ausencia y tipo de cubierta que tenga el nanomaterial.

Los investigadores deberán formar recursos humanos de alto nivel, con la capacidad de innovar y ofrecer alternativas tecnológicas de punta pero, será conveniente también, que esos recursos humanos recién formados consideren como puntos críticos de interés lo relacionado con el cuidado del medio ambiente y el bienestar social. De otra forma, se podría cometer el error de formar recursos humanos que produzcan materiales que comprometan la salud humana o ambiental y en este sentido, históricamente hay muchos ejemplos, basta con mencionar el DDT, el asbesto o un sinnúmero de medicamentos, los cuales luego de ser 'evaluados científicamente' fueron retirados del mercado por sus efectos secundarios, tóxicos o carcinogénicos.

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10.2.3 Capítulo de libro. Nanotechnology in crop protection: Status and future trends. Publicado en: Nanobiopesticides Today and future perspective. Elsevier

CHAPTER

Nanotechnology in crop protection: Status and future trends

2

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2.1 Introduction

Nanotechnology is the study and design of materials at nanoscale dimensions, that is, 1–100 nm. Over the last 20 years, the development of new products using nanoparticles (NPs) has become a scientific and technological priority worldwide (León-Silva et al., 2016). This is due to their novel properties, such as high surface area to volume, cation exchange capacity and complexation, increased reactivity, unusual structure, large ion adsorption ratio, and great stability and aggregation abilities (Carrillo et al., 2015; Nel et al., 2006; Sharon et al., 2010). These characteristics make the new product different than the original form of molecules and bulk materials used (Guo, 2004; Li et al., 2001). NPs, nanomaterials or nanodevices, have been developed in several industrial fields such as medicine, electronics, energetic, genetic, and aeronautical, among others.

More than 60% of the population in developing countries depends on agriculture for sustenance (Brock et al., 2011). The FAO (2013) has stated that food and agriculture nanotechnology must emphasize: (i) smart release of active ingredients; (ii) disease management and crop protection (Liu et al., 2006; Sahayaraj et al., 2016); (iii) diminution of the loss of nutrients during fertilization and increasing the fertilization process (Hossain et al., 2008; Liu and Lal, 2014); and (iv) production of bio-nano compounds from traditional crops (Parisi et al., 2015). Additionally, there is the necessity to increase food production for an ever-growing population, which is projected to reach 7.7 billion by the end of 2018 (World Bank, 2015).

Today, agricultural researchers are seeking sustainable and less aggressive alternatives to fight plagues and diseases; utilize limited resources such as water, soil, and nutrients; and decrease environmental pollution in rural areas (Medina-Perez et al., 2018).

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Finding new and low-cost investments in research and innovation in nanotechnology applied to crop production could be a significant contribution to this effort (Medina-Perez et al., 2019). The application of new genetic tools, precision agriculture, specific tissue cultures, fertilization, and nanobiotechnology could help to understand crop-biological responses to nanomaterials. This could ultimately be useful in increasing the yields and improving the food quality in order to offer affordable, healthy, and innocuous food worldwide (Prasad et al., 2010; Tarafdar et al., 2013).

NPs may have different functionality, benefits, or even toxicity in the plant system (Medina-Perez et al., 2018, 2019). It would depend on their nature, size, shape, aggregation, dose, the plant or soil condition, or the application strategy (Lee et al., 2008; Lin and Xing, 2008; Raliya et al., 2016; Seeger et al., 2009; Sunada et al., 2008). Some NPs have been documented to stimulate antimicrobial (Chen and Chiang, 2008; Singh and Nalwa, 2011) and antifungal activity (Kumari and Yadav, 2014) in microorganisms, suggesting their potential to control pests and crop diseases.

The applications of nanotechnology in crop protection are diverse but they are mainly used for the elaboration of slow-release encapsulated agrochemicals. New nanomaterials have been developed utilizing metallic, polymeric, and inorganic nanoparticles that are intended to improve intelligent nanosystems with the ability to capture and immobilize nutrients and permit their gradual release in the soil to increase fertilizer efficiency. Besides, the development of nanosensors allows the detection of the presence of pests and diseases in crops (Dubey and Mailapalli, 2016; Fraceto et al., 2016). Several types of metallic nanoparticles such as Ag, Fe, Cu, and Zn may be used with a dual approach: as nanofertilizers improving the germination of seeds and promoting the growth of plants, and as pesticides or fungicides against some pathogenic microorganisms and plagues (Le Van et al., 2016).

With respect to food conservation and prevention of losses, nanotechnology has allowed for the development of smart packaging of foods that can reveal the presence of bacteria or fungi (Joyner and Kumar, 2015) while also extending the shelf life of horticultural products by reducing pathogens. For example, this includes the addition of hydroxyl radicals by electrospraying used on surfaces and some metallic nanoparticles such as TiO NPs used for pathogen control by generating reactive oxygen species (ROS) upon irradiation. Other metallic NPs such as Ag NPs or ZnO NPs that cause bacterial cell damage (ROS) are also often used. Designing nanostructured materials to be used on surfaces can avoid the adhesion of microorganisms (Rodrigues et al., 2017). Overall, the objective of this chapter is to discuss the status and future trends regarding nanoscience and nanotechnology in crop protection.

2.2 Nanoscience and Nanotechnology as Useful Tools in Agriculture

Nanoscience and nanotechnology are the most transcendent modern tools in agriculture and will become an economic force in the future. By providing new agrochemicals and ways to deliver active compounds, nanotechnology offers the possibility to reduce and optimize the use of conventional products, such as toxic pesticides. Its applications include: (a) pesticides and fertilizers formulated for crop improvement, (b) applications of nanosensors and nanobiosensors to detect pathogens or hazardous residues; (c) nanocarriers to improve genetic manipulation of plants and beneficial microorganisms; (d) plant disease diagnostics, (e) animal health and production, and (f) postharvest handling. According to the FAO (2013), it will be necessary to increase food production by 70% by the year 2050. Nanotechnology can supply the tools needed in modern agriculture to solve future problems of food security and energy demand with a sustainable approach (Fig. 2.1).

Encapsulated and entrapped nanocomposites can control the liberation of small amounts of active compounds so they can be rationally assimilated by the crop during growth, without overdoses, and with less input and waste (Chen and Yada, 2011). Nanoscale vehicles designed to reach the roots can improve the uptake of beneficial molecules or active compounds and can also look for target soil particles and repair damage (Johnston, 2010). These active compounds can be: (i) herbicides (Goldwasser et al., 2003; Grillo et al., 2010, 2012), (ii) fertilizers (Bin Hussein et al., 2002; Corradini et al., 2010; Derosa et al., 2010; Kottegoda et al., 2011a,b), (iii) pesticides (Mishra and Singh, 2014; Nuruzzaman et al., 2016), or (iv) growth promotors (Peteu et al., 2010). Additionally, the careful administration of these compounds can reduce the need for soil and water treatment applications (Mukhopadhyay, 2014), hence mitigating climate change (Solanki et al., 2015).

The development of water-retaining nanomaterials such as nanoclays, nanozeolites, and nanohydrogels is well known (El Salmawi, 2007). Nanoclays made from a polyacrylamide nanocomposite have high water retention and water absorption

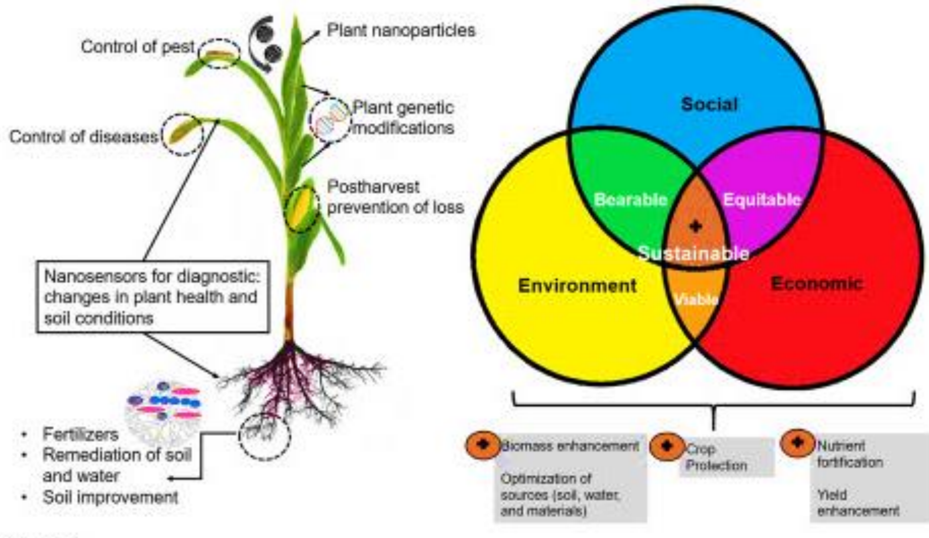

FIG. 2.1

Advances in sustainable applications of nanotechnology and nanoscience.

capacities when coated with zinc and can be applied to rain-fed crops (Jatav and De, 2013). Mahfoudhi and Boufi (2016) designed nanohydrogels made of cellulose nanofibrils and polyacrylic acid-*co*-acrylamide, obtaining a structure that induced the release of urea in the system, simulating a fertilizer with novel properties (Sekhon, 2014).

Nanotechnology has also been developed in animal production, for example, in drug delivery systems, the diagnosis and treatment of diseases, and animal nutrition (Zhao et al., 2017). There are lines of nanoadditives and antimicrobial nanoemulsions that prevent diseases in farm animals as well as nanocomposites for packaging of food (Ganjigohari et al., 2018). Introducing nanoadditives in animal diets can promote growth, health, and meat quality; the nanocarriers transport active ingredients and beneficial microorganisms to animal systems. Minerals such as selenium, copper, iron, and zinc could be incorporated in crops and in animal diets by nanoparticles (Hill and Li, 2017).

Nanosensors have a range of 1–100 nm and are ingenious tools for diagnostics of plant and soil conditions in agriculture. These nanoparticles provide a large reaction surface area, prompting a rapid reaction response because of the increased sensitivity to detect signals. This makes them more efficient than biological and chemical methods. These nanodevices can be used to detect microorganisms, pollutants, and changes in the freshness of food (Vanderroost et al., 2014). The use of nanosensors or biosensors can be an advantage to improve agricultural precision in the future.

2.3 Nanofertilizers for Healthy Crops

It is obvious that healthy crops have a built-in capacity to prevent pest attacks. Therefore, before using a biopesticide, the use of biofertilizers should be the priority. Traditional inorganic fertilizers are used to increase the quality and yield of crops. Nevertheless, the hazardous impact on soil due to the toxic nature of these chemicals affects the fertility, microbial population, and mineral content of the soil, which subsequently decreases the crop yields (Ditta and Arshad, 2016; Prasad et al., 2017). It has been documented that >50% of chemical fertilizers are lost by leaching, bioconversion, and mineralization. Additionally, intensive agriculture requires the simultaneous management of insects, diseases, and weeds, and as a result, the impact on the ecosystem is multiplied due to the resistance of insects, pathogenic microorganisms, and weeds to treatments with antibiotics, pesticides, and herbicides (Gadanakis et al., 2015). The gradual introduction of nanotechnology in agriculture over the last decade has established nanofertilizers and nanopesticides as sustainable methods for precision farming. Several engineered and natural nanoparticles and the nanoencapsulation of nutrients in polysaccharide, mineral, or liposome nanocapsules have been developed to optimize the traditional dosages to more balanced doses. Consequently, this has reduced the regular costs of agrochemicals for crop protection as well as the expenses of treatments to restore the environment (Chhipa, 2017). A great future is foreseen through the research and application of nanoscale studies of biological materials originating from agriculture in the search for a sustainable society (Faunce et al., 2008; Panpatte et al., 2016). The development of smart systems for the liberation of nanocompounds could be a challenge for the next decade.

Nanofertilizers are bulk or nano-sized materials, mostly nutrients, that can be extracted from several parts of plants and can enhance growth and improve the production and yield. Like traditional fertilizers, nanofertilizers can be applied directly to soil or foliage. The small size of the particles allows them to get into the pores of roots and leaves; other favorable characteristics are their reactivity and solubility (Dubey and Mailapalli, 2016; Naderi and Danesh-Shahraki, 2013).

The effects of the application of nanoparticles are both negative and positive. Some authors mentioned that the impact of NPs on plant growth can be related to their concentration, size, and the inherent properties of the element involved. This depends on the physiological and biochemical functions that such a component or compound plays in the plant; it may act as a micronutrient, as in the case of copper or zinc (Wang et al., 2015). Some reports on the application of nanoparticles, mainly nanofertilizers, in different crops have shown that they increased the plant growth, nutritional content, and enzymatic activity (Ditta et al., 2015; Liu and Lal, 2015; Chhipa, 2017). Adverse effects have also been documented; some authors reported that phytotoxicity generates unpredictable and irregular behavior on oxidative stress, which in turn depends on the type, concentration, properties, and means of exposure of NPs (Foltête et al., 2011; Gómez et al., 2017).

Some products known as nanofertilizers have already been commercialized. Several examples are: (i) Nano-GroTM (plant growth regulator and immunity enhancer); (ii) nano-Ag AnswerR (microorganisms, mineral electrolyte, and sea kelp), (iii) TAG NANO (NPK, PhoS, Zn, Ca, etc.), (iv) protein lactogluconate, and (v) others such as micronutrients, probiotics, vitamins, seaweed extracts, and humic acid, among others (Prasad et al., 2017).

There are three categories of nanofertilizers, depending on the plant's nutrient requirement: macronanofertilizers, micronanofertilizers, and nanoparticulated (Fig. 2.2). Macronanofertilizers contain nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sulfur (S), and calcium (Ca) encapsulated in nanoparticles; they increase the uptake of nutrients in plants (Tarafdar et al., 2013, 2016). Micronanofertilizers, that is, ZnO and CuO NPs, showed effects on the reactivity of phytohormones by increasing the growth rate in plants (Wang et al., 2012, 2015). Another study concluded that the addition of ZnO and CeO_2 NPs to cucumber plants (*Cucumis sativus*) changed the starch and carbohydrate content of the fruits (Zhao et al., 2013). Zinc oxide NPs were studied for their antimicrobial activity (Fang et al., 2013; Sabir et al., 2014) and for their potential as nanofertilizers promoting germination, growth, and development (Dimkpa et al., 2015a; Naderi and Danesh-Shahraki, 2013; Prasad et al., 2012; Raskar and Laware, 2014; Siddiqui et al., 2015). Delfani et al. (2014) found that Fe NPs increased the chlorophyll content in the leaves of the black-eyed pea and Ghafariyan et al. (2013) found similar results in *Glycine max*. Raliya and Tarafdar (2013) reported that ZnO

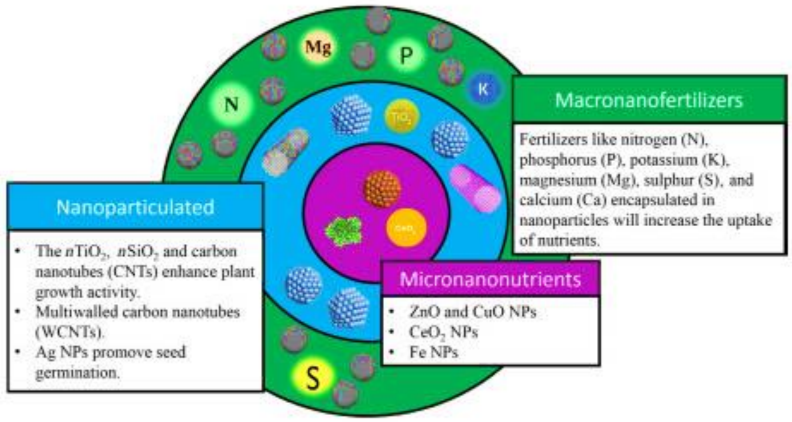

FIG. 2.2

Categories of nanofertilizers applied to agriculture crops.

NPs induced significant improvement in *Cyamopsis tetragonoloba* biomass, shoot and root growth, root area, chlorophyll content, and protein synthesis. Microbial population, acid phosphatase, alkaline phosphatase and phytase activity in the rhizosphere were also improved significantly.

Finally, nanoparticulated, commonly $nTiO_2$, $nSiO_2$, and carbon nanotubes (CNTs), enhance plant growth activity. Nano-sized TiO_2 had a positive effect on the growth of spinach when applied to the leaves (Gao et al., 2006; Hong et al., 2005; Rezaei et al., 2015; Yang et al., 2006; Zheng et al., 2005). Nano-SiO_2 increased leaf biomass, proline content, and chlorophyll (Haghighi et al., 2012; Kalteh et al., 2014); TiO_2 and SiO_2 improved nitrogen fixation in *G. max* and favorably influenced seed germination and growth (Lu et al., 2002). Titanium oxide application in barley (*Hordeum vulgare* L.) resulted in an increment in seed yield while titanium dioxide nanoparticles (0.02%) were more effective in improving yield. The highest seed yield was obtained when nonstressed plants under water-deficit stress conditions were treated with titanium dioxide nanoparticles (0.02%) during the stem elongation stage (Jaberzadeh et al., 2013).

Carbon nanotubes actively interact with plants, displaying promoter activity. Carbon nanotubes have been used to fertilize several vegetables such as tomatoes, cabbage, carrots, onions, cucumbers, soybeans, and corn, and in all cases, an increase in plant growth and yield was observed (Cañas et al., 2008; Khodakovskaya et al., 2012; Lin and Xing, 2007) while water uptake capacity was better in some plants (Srinivasan and Saraswathi, 2010). Tomato plants (*Lycopersicum esculentum*) showed changes in aquaporins regulation in response to stress (Khodakovskaya et al., 2009). Multiwalled carbon nanotubes (MWCNTs) have enhanced the growth of some crops (Giraldo et al., 2014; Khodakovskaya et al., 2012). Some authors reported an inhibitory effect of MWCNTs in plant growth (Begum et al., 2014; Ikhtiari et al., 2013; Tiwari et al., 2014).

Silver NPs have mostly been reported to have adverse effects on plant growth, although several studies have demonstrated the contrary (Salama, 2012; Yin et al., 2012; Syu et al., 2014). Rico et al. (2015) reported increased plant height, chlorophyll content, dry biomass, and yield when Ag NPs were applied to plants. On the other hand, it has been indicated that, in low concentrations, Ag NPs have a positive effect on seed germination and the promotion of plant growth. Sharma et al. (2012) reported that Ag NPs promoted the growth of mustard seedlings (***Brassica juncea***) in concentrations of 25 and 50 mg/L, which was reflected in the greater root length, dry biomass, and height of the plants. However, at high concentrations (250–500 mg/kg of soil), these NPs inhibited the germination and growth of bean plants (Dimkpa et al., 2015b). In a recent study, Ag NPs were used to improve the yield of ***Pisum sativum*** L. They were synthesized by a green method using ***Berberis lycium*** Royle extract. The work showed that Ag NPs had a defined capacity to improve crop growth and yield (Mehmood and Murtaza, 2017). Similarly, a nanocrystalline silver colloidal solution containing polyhexamethylene biguanide hydrochloride (PHMB) was obtained by reduction of silver nitrate with sodium borohydride. It demonstrated positive effects on the agronomic properties of potatoes, wheat, and apples, and induced increased enzymatic activity of peroxidase and catalase in plant tissues (Krutyakov et al., 2017).

Copper NPs were used as a growth promoter in the field, promoting a significant increase in height, root length, fresh and dry mass, and the yield index of crops (Shende et al., 2017). Another contemporary application of Cu NPs is combined with chitosan-PVA hydrogels to improve and intensify the capsaicin content in pepper. This application increased capsaicin content by 51% compared to the control and also increased ABTS antioxidants [2,2-azino-bis (3-ethylbenzothiazolin-6-sulfonic acid)] and DPPH (2,2-diphenyl-1-picrylhydrazyl), total phenols, and flavonoids in the fruits (Pinedo-Guerrero et al., 2017).

Nanocomposites were developed to polymerize paraformaldehyde with urea extruded with montmorillonite, thus controlling the release of urea and decreasing the volatilization of NH_3, a very useful feature in oxisol soils (Pereira et al., 2017). In another study with urea and phosphate where the nanocomposites were developed with mixtures of thermoplastic starch and urea as a matrix, hydroxyapatite particles were dispersed, providing a more controlled release of the compounds (Giroto et al., 2017). All the above-mentioned studies show the importance of nanofertilizers for crop health that could increase the vigor of the crops to withstand the impact of pests and diseases before the application of pesticides/biopesticides.

2.4 Nanotechnologies for Insect Pest Control

The yearly estimated losses inflicted by pest infestation are about 26%–30% in barley, sugar beet, wheat, soybean, and cotton; 40% in rice; 39% in potatoes; and 35% in maize (Oerke and Dehne, 2004). Pimentel (2009) stated that pest insects cause about a 13% loss in crops and to control pests, about 3 billion kg of pesticides are applied each year. The main issue with chemical pesticides is that they are not biodegradable and are extremely toxic to nontarget animals such as insect pollinators, birds, fish, amphibians, and humans (Gill and Garg, 2014). By developing nanopesticides, the intention is to avoid or eliminate the use of pesticides made from potentially toxic chemical compounds (de Oliveira et al., 2014; Madbouly et al., 2017; Ureña-Saborio et al., 2017) because these chemicals are linked to modifications in pests, triggering resistance and negative impacts on the environment (Campolo et al., 2017; Krutyakov et al., 2017).

With respect to agricultural pest control through nanotechnology, little is documented. The mechanism of action of nanosilica (~3–5 nm) in pest control is based on their absorption into the insects' cuticular lipids, and then the consequent death of the insect caused by desiccation when nanosilica are applied on the leaves and stem surface (Ulrichs et al., 2006). Amorphous nanosilica particles were tested on two stored grain insects, ***Sitophilus oryzae*** and ***Tribolium castaneum***, and two field insects, ***Lipaphis pseudobrassicae*** and ***Spodoptera litura***; they were found to be competent pesticides (Goswami et al., 2010). Debnath et al. (2011) reported that silica NPs were effective against ***Sitophilus oryzae***, resulting in 90% mortality of *S. oryzae* adults after a 2-day application of a 2 g/kg dose. Biogenic silver nanoparticles synthesized by swallow grass leaf extract (***Euphorbia prostrata***) were used against *S. oryzae*, causing 100% mortality after a 7-day treatment (Abduz Zahir et al., 2012). Bharani and Namasivayam (2017) found similar results when Ag NPs obtained from pomegranate extract were used against a polyphagous pest, *S. litura*. Santhoshkumar et al. (2012) evaluated the activity of veld grape (***Cissus quadrangularis***) vine extract for synthesis of Ag NPs to protect against adult flies (***Hippobosca maculata***); the results indicated a 100% mortality rate after applying a concentration of 25 mg/L. Additionally, green-fabricated Ag NPs by ***Saponaria officinalis*** root extract showed evidence of acaricidal and antiovipositional activity in all developmental stages of a polyphagous pest, ***Tetranychus urticae*** (Pavela et al., 2017). Stadler et al. (2010) indicated that the insecticidal activity of nanostructured alumina on two stored food pests, *S. oryzae* and ***Rhyzopertha dominica***, in wheat resulted in significant mortality in 3 days.

Some nanomaterials showed smart properties, such as slow liberation, for a safe delivery of compounds such as pesticides and fertilizers (Forgiarini et al., 2001; Kuzma and VerHage, 2006). Nanoparticles can be loaded with pesticides, improving their solubility and controlling the liberation of active ingredients, as shown in Fig. 2.3 (Debnath et al., 2011; Kah et al., 2013; Lauterwasser, 2005; Scrinis and Lyons, 2007). Barik et al. (2008) and Kah et al. (2013) reviewed several nanoencapsulation methods: microemulsion, nanoemulsion, nanodispersion, polymer-based NPs, solid lipid NPs, clay, layered double hydroxides, and metal-based nanoparticles; see Table 2.1.

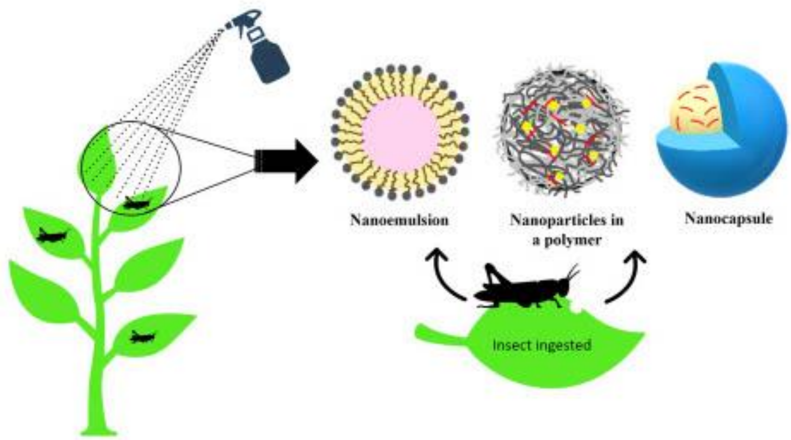

FIG. 2.3

Nanomaterials used in pest insect control.

Table 2.1 Examples of Nanoparticles Loaded With Active Ingredients

Nanoparticle	Active Ingredient	Benefits	Reference
Amphiphilic modified-*N*-(octadecanol-1-glycidyl ether)-*O*-sulfate chitosan (NOSCS)	Rotenone (insecticide for control of aphids, thrips, acaroid)	Increased activity of rotenone to 13,000 times more than free rotenone in water	Lao et al. (2010)
Nano and microemulsion system (oil in water)	β-Cypermethrin (β-CP)	Improved stability of the sprayed solution	Wang et al. (2007)
Polyethylene glycol-coated nanoparticles	Garlic essential oil	Control of adult *Tribolium castaneum* with 80% efficiency	Yang et al. (2009)
Porous hollow silica nanoparticles (PHSNs)	Validamycin (pesticide)	Prolonged release as needed by plants	Liu et al. (2006)
Alginate	Azadirachtin	Neem oil nanoemulsion	Jerobin et al. (2012)
Alginate (emulsion)	Imidacloprid	Cytotoxicity in sucking pest (leafhoppers)	Kumar et al. (2014)
Polyacetic acid-polyethylene glycol-polyacetic acid	Imidacloprid	Slow liberating nanocapsules	Memarizadeh et al. (2014)
Synthesized 6-*O*-carboxymethylated with anchorage of ricinoleic acid	Herbal insecticide azadirachtin	Improved control of the degradation rate and the release of the insecticide	Feng and Peng (2012)
Nanocapsules and nanospheres of poly-(ε-caprolactone) polymer	Extracts of neem (*Azadirachta indica*) and azadirachtin	The nanoformulations showed high entrapment efficiency—529cy (>95%) and UV stability (30 times more compared to conventional products)	Forim and Fernandes (2011)

2.5 Nanotechnologies for Plant Disease Control

Plant pathogenic bacteria and fungi have acquired resistance against conventional pesticides. This has led to the search for more efficient active compounds, especially in the case of plant pathogenic fungi, owing to their great adaptability to environmental changes (Gill and Garg, 2014). The growing demand for food production directly contributes to the use of 2 million tons more pesticides worldwide each year: 24% in the United States, 45% in Europe, and 31% in the rest of the world (Abhilash and Singh, 2009). Only a small amount (0.1% approximately) of about 3 million tons of active ingredients in pesticides effectively works in crop protection; the rest (99.9%) is lost through the application method (air, soil, water), deposition, and photodegradation (Castro et al., 2014; Tilman et al., 2002).

The nanoencapsulation of pesticides and beneficial microorganisms is a favorable way to control pests and diseases and reduce the number of residues that cause damage to the environment. Applied in this context, these systems are capable of minimizing leaching and at the same time improving the absorption of nutrients by plants and mitigating eutrophication, thus reducing the transfer of nitrogen to aquifers (Liu and Lal, 2015). In addition, it is important to mention that nanomaterials could also be exploited to improve the structure and function of pesticides by increasing solubility and resistance to hydrolysis, improving photo-decomposition, and/or providing a more efficient and controlled release toward target organisms (Grillo et al., 2016; Mishra et al., 2014). Research in nanotechnology agriculture is advancing because its potential benefits could enhance the quality and yield of the crops. Several examples of nanoparticles used in plant disease control are listed in Table 2.2.

2.6 Metallic Nanoparticles

Metallic nanoparticles such as silver nanoparticles interact with cell membranes. Silver ions are widely known for their high reactivity and destabilizing affects on bacterial and fungal cell membranes, hence their use to combat human pathogens (Nomiya et al., 2004). Although their mechanism of action is not yet fully understood, it is known that silver ions interact with the thiol group (–SH) (Feng et al., 2000), causing cell rupture (Matsumura et al., 2003). In the case of silver nanoparticles, they produce changes in the permeability of membranes, affecting the respiration of the cells (Narayanan and Park, 2014). Lamsal et al. (2011) showed that Ag NPs inhibited the activity of ***Colletotrichum*** spp. (anthracnose causing pathogen) in cultivated cucumber and pumpkin in a field trial. They also found that the treatment with Ag NPs was more effective than bulk Ag treatment. A big concern is the possible translocation and compartmentalization of Ag NPs applied to leaves, which can potentially be introduced to humans through the trophic chain (Larue et al., 2014).

Massive quantities of copper are found in fungicides, algaecides, and herbicides, and this plays an essential part in the control and prevention of plant disease (de Oliveira-Filho et al., 2004). Copper-based fungicides produce reactive hydroxyl

Table 2.2 Nanomaterials That Are Used for Plant Disease Management

Pathogen	Nanoparticle	Disease Controlled	Reference
Bacillus megaterium, *Pseudomonas syringae*, *Burkholderia glumae*, and *Xanthomonas oryzae*	Silver nitrate	Bacterial blight in different plant species	Velmurugan et al. (2012)
Xanthomonas campestris pv.	Nano silver	Significant reduction of cabbage black rot in a pot experiment	Gan et al. (2010)
Xanthomonas axonopodis pv. punicae	Nano copper	Pomegranate bacterial blight	Mondal and Mani (2012)
Xanthomonas perforans	Silver nanoparticles on graphene oxide Formulations of titanium oxide with silver and zinc	Bacterial spot of tomatoes	Ocsoy et al. (2013) and Paret et al. (2013)
Rhizopus sp. *Colletotrichum capsici*, *C. gloeosporioides* *Aspergillus niger*	Chitosan	Mycelial growth delayed in fungi	Chookhongkha et al. (2013)
Sclerotinia homoeocarpa	Zinc oxide and silver	Dollar spot on cool-season turfgrasses	Li et al. (2017)
Fusarium solani and *Venturia inaequalis*	Silver-doped titanium oxide	Fusarium (wilt in crops such as tomato, potato, etc.) and apple scab disease caused by *V. inaequalis*	Boxi et al. (2016)
Rhizoctonia solani and *Neofusicoccum parvum*	Silver nanoparticles	Collar rot, root rot, damping off and wire stem caused by *R. solani*; Severe decline and dieback symptoms in grapevines caused by *N. parvum*	Khatami et al. (2016)
Gloeophyllum abietinum, *G. trabeum*, *Chaetomium globosum*, and *Phanerochaete sordida*	Silver nitrate	Phytopathogenic wood decay	Narayanan and Park (2014)

Continued

Table 2.2 Nanomaterials That Are Used for Plant Disease Management—cont'd

Pathogen	Nanoparticle	Disease Controlled	Reference
Aspergillus flavus var. *columnaris*	Silver nitrate	Inhibition of the aflatoxigenic pathogen growth	Yassin et al. (2017)
Setosphaeria turcica	Ag nitrate	Northern corn leaf blight	Huang et al. (2017)
Alternaria solani and *Fusarium oxysporum*	Cu-chitosan	Early blight on foliage, collar rot on basal stems of seedlings, stem lesions of adult plants and fruit rot caused by *A. solani*; wilt and rots on agricultural and ornamental plants by *F. oxysporum*	Saharan et al. (2015)
Nigrospora sphaerica, *Botryosphaeria dothidea*, *Nigrospora oryzae*, and *Alternaria tenuissima*	Oleoyl-chitosan	Damage to leaf caused by *N. sphaerica*; cankers on a wide variety of tree and shrub species caused by *B. dothidea*; grain spots induced by *N. oryzae* and nailhead spot of tomato by *A. tenuissima*	Xing et al. (2016)
Fusarium graminearum	Chitosan CS with tripolyphosphate	Fusarium head blight (FHB) on wheat	Kheiri et al. (2017)
Alternaria solani sorauer, *Fusarium oxysporum* f.sp. *vasinfectum*, and *Fusarium moniliforme*	Coumarin-chitosan derivatives	Early blight in tomato produced by *A. solani*, withered cotton leaves as a result of *F. oxysporium*, and stem rot and root rot in crops such as corn, wheat, and rice caused by *F. moniliforme*	Yang et al. (2018)

radicals, which could damage biomolecules such as lipids, proteins, and DNA, among others. Several studies have confirmed that copper nanoparticles have antimicrobial activity against a wide spectrum of plant pathogenic bacteria and fungi. Giannousi et al. (2013) used different dimensions (11–14 nm) and chemical forms (Cu_2O, CuO, and Cu/Cu_2O) of copper nanoparticles in a greenhouse on tomato plants (***Lycopersicon esculentum***) to fight ***Phytophthora infestans***. They found that the Cu NPs had greater effectiveness in lesser quantities compared to other registered products, without any apparent damage to the tomato plants. Brunel et al. (2013) developed a chitosan nanogel complex with copper and derived that they had a robust synergistic effect in inhibiting the growth of the plant pathogenic fungus *Fusarium graminearum*. Esteban-Tejeda et al. (2009) used low melting point soda-lime glass powder as a vehicle for copper nanoparticles and demonstrated that this combination had a synergistic effect on antimicrobial activity, inhibiting yeasts and gram-positive and -negative bacteria while releasing calcium ions that further heightened the inhibitory effect.

Zinc oxide nanoparticles have a broad range of uses, owing to their unique properties such as a wide band gap; antimicrobial, optical, and catalytic efficiency; and a large active surface area (Hussain et al., 2016). The antibacterial and antifungal activities of zinc nanoparticles have been explained in previous studies. Zinc NPs produce free radicals that prompt oxidative stress damage in cell membranes (Brayner et al., 2006). Little is known about the effects of ZnO NPs on phytopathogenic fungi. Zinc nanoparticles appear to influence the morphology of fungal structures, as reported by He et al. (2011), where two phytopathogenic postharvest fruit molds, *Botrytis cinerea* and *Penicillium expansum*, were controlled by ZnO NPs (70 nm). Zinc oxide NPs caused deformation of the fungal hyphae and production of conidiophores, which ultimately led to the death of the hyphae in *Aspergillus flavus* and *A. niger* (Jayaseelan et al., 2012). Titanium dioxide NPs release chemically reactive free radicals (hydroxyl and superoxide radicals) when they are exposed to light, a photocatalytic process that affects a wide range of microorganism cells (Choi et al., 2010; Lu et al., 2006; Owolade and Ogunleti, 2008; Tsuang et al., 2008; Wu et al., 2010). When TiO_2 nanoparticles are doped with zinc, silver and copper it can boost their functional properties (Colón et al., 2006; Namiki et al., 2005).

2.7 Biopolymer Nanoparticles

Chitosan is a polymer of biological origin obtained by the *N*-deacetylation of chitin. It is nontoxic, antimicrobial, and biodegradable and has extensive application in agricultural nanotechnology (Yang et al., 2018). Its antimicrobial activity is explained by the strong interaction of its cationic amino groups with cellular components. However, due to its low solubility, chitosan has been chemically modified to triethylenediamine dithiocarbamate chitosan and *o*-hydroxyphenylaldehyde thiosemicarbazone, which, unfortunately, reduced its biodegradability and increased its toxicity (Xing et al., 2016). Nevertheless, chitosan nanoparticles have been shown to have exciting versatility and permeability to biological membranes and are harmless to humans. Some authors have presented works in which chitosan nanoparticles were used in combination with other nanoparticles. Saharan et al. (2015) mixed Cu NPs and chitosan nanoparticles to amplify their antifungal action against *Alternaria solani* and *Fusarium oxysporum* mycelia growth in vitro. They also carried out pot experiments to evaluate the effect of Cu-chitosan NPs on early blight and tomato fusarium wilt disease. Kheiri et al. (2017) used chitosan NPs for their antifungal activity against *Fusarium graminearum*, which attacks wheat. This resulted in fungal growth suppression, suggesting that these particles can potentially replace conventional chemicals.

2.8 Pathogen and Postharvest Disease Control Using Nanotechnologies

All over the world, a substantial amount of food is lost, pre- and postharvest, due to decomposition. About 30%–50% of food derived from agriculture in Europe and North America is wasted at any stage of the market chain. In most cases, these losses are the result of degradation by bacteria and fungi (Rodrigues et al., 2017). As the world is faced with a growing population and a demanding need for more food, nanotechnology could also be an essential tool in the management and reduction of postharvest losses. Various nanotechnological products can be utilized in postharvest handlings, such as nanofilms and nanosensors, to extend the postharvest life of fruits and vegetables.

For example, Chookhongkha et al. (2013) used chitosan NPs to alter the mycelial growth of several fungal species to improve chili seed quality. Chitosan polymer and chitosan nanoparticles at a concentration of 0.6% (w/v) significantly delayed the mycelial growth of *Rhizopus* sp. *Colletotrichum capsici*, *C. gloeosporioides*, and *Aspergillus niger* compared to concentrations of 0.15% (w/v) and 0.2% (w/v) chitosan nanoparticles and the control. The seed coating did not significantly affect the moisture content, germination index, or mean germination time when compared to the control samples.

Mohammadi et al. (2016) studied the effects of the nanochitosan films encapsulated in *Cinnamomum zeylanicum* essential oil during the storage of cucumbers (*Cucumis sativus*) to protect against *Phytophthora drechsleri*, a common pathogen during storage. The coated fruit was firmer and maintained its color and water content while also showing lower microbial counts ($P < .05$) throughout storage. Chitosan mixed with other nanoparticles has also been studied. Yu et al. (2012) made a 1% chitosan film with 0.04% nanosilicon dioxide. They measured the quality properties of harvested jujube after a 32-day storage at ambient temperature and found that coated fruits showed less decay incidence and lower respiration rate and weight loss.

Shi et al. (2013) studied the same compound in longan fruits at room temperature and discovered that the coating improved the shelf life of the fruits by reducing the browning index, decreasing weight loss, and inhibiting the amount of malondialdehyde and polyphenol oxidase activity. Hu et al. (2011) developed a nanocomposite-based packaging by blending polyethylene (PE) with nano-Ag, nano-TiO_2, and montmorillonite, then applied it to kiwifruit during a 42-day storage period. They reported that spore germination was inhibited in coated fruit and that changes such as weight loss, softening, color variation, and solid soluble content of kiwifruit were significantly reduced by 22.67%, 124.84%, 23.46%, and 14.42%, respectively. Therefore, this indicated a possibly positive effect of the film on the maturation process of the kiwi fruit.

Silver nanoparticles or nanosilver (2.5 nm) have been used as antimicrobials. Pulse and vase solution treatments have been studied over the years. Liu et al. (2009) demonstrated that treatment with a nanosilver solution (5 mg/L) pulsed for 24 h inhibited bacterial growth and extended the vase life of cut gerbera (*Gerbera jamesonii* cv. ruikoi) stem compared to the control, which was sonicated with water, during the first 2 days. Solgi et al. (2009) evaluated the effects of silver nanoparticles on *Gerbera jamesonii* cv. "Dune," finding significantly higher relative fresh weight than the control.

Hassan et al. (2014) applied biologically synthesized Ag NPs and showed that the application of pulse treatments at concentrations of 25, 50, and 100 mg/L for 24 h improved the postharvest quality of cut rose flowers cv. "First Red." All levels of Ag NPs had significant effects on the vase life of flowers. The microbial growth was suppressed in the vase solution compared to the control with only water.

Conventional fruit-coating material combined with a solution of nanosilver at 1% concentration inhibited the growth of *C. gloeosporioides*, associated with mango anthracnose, and significant disease reduction was exhibited compared to control (Yadollahi et al., 2010). Recently, there have been several published works on the development of nanolaminate coatings and how they can be incorporated into functional nanoparticulated nanomaterials to be used as carriers of additives or active ingredients (Gholami et al., 2017; González-Reza et al., 2018; Xu et al., 2018). Nanolayer systems, though possessing a variety of features, are still scarcely studied.

2.9 Future Perspectives and Challenges

There is a need to move toward more ecological methods in the development of nanomaterials. These include the use of biological entities or their derivatives (Baker et al., 2017); making experimental designs with a realistic approach; and changing in vitro testing experiments to field trials to encourage environmentally friendly nanotechnologies to achieve agricultural benefits. In order to utilize the environment friendly nanotechnologies in agriculture, it is required to validate safe doses of nanoparticles, which in most cases are not yet defined. This validation can be achieved by taking trans-generational effects into account through long-term in situ field trials, carrying out studies on trophic chain transfer, and examining the relationship between nanoparticle-insect, nanoparticle-plant, and nanoparticle-microorganism interactions. This will allow to understand the real effects of nanoparticle applications and help in reducing and avoiding environmental risks (Mishra et al., 2017).

An interesting work was published by Hawthorne et al. (2014) where they evaluated the trophic transfer of bulk and nanoparticles of CeO_2 through a terrestrial food chain. Zucchini (*Cucurbita pepo* L.) was planted in soil amended with 0 or 1228 μg/g bulk CeO_2 and CeO_2 NPs. The cerium content in zucchini leaf tissues was determined after 28 days by ICP-MS and, at the same time, leaves from each treatment were fed to crickets (*Acheta domesticus*). After 14 days, some crickets were analyzed for Ce while the others were fed to wolf spiders (of the Lycosidae family), and their Ce content was determined later. The Ce content in the zucchini, crickets, and spiders was significantly greater when the exposure was to the nanoparticles. The zucchini leaves that were exposed to bulk CeO_2 contained 707 ng/g Ce while crickets fed with nanoparticulated CeO_2-exposed zucchini leaves contained significantly more Ce (33.6 ng/g) than the control or bulk-exposed insects (15.0–15.2 ng/g). Feces from control, bulk, and NP-exposed crickets contained Ce 248, 393, and 1010 ng/g, respectively. Spiders that consumed crickets from control or bulk treatments contained undetectable amounts of Ce; NP-exposed spiders contained Ce at 5.49 ng/g. The study proved that CeO_2 NPs can accumulate in zucchini tissues at high enough levels to be measured and that trophic transfer and possible food chain contamination could result.

Inorganic pesticides are the most used tool in pest control, but as we have seen, their use in large doses can induce pest resistance and cause environmental contamination. Hence, a focus on developing new compounds, such as polymers as carriers and organic actives of botanical origin that are as effective as existing inorganic pesticides, should be a priority in the future. In recent years, many studies have focused on environmentally friendly nanotechnologies. Campos et al. (2018) prepared and characterized chitosan nanoparticles functionalized with β-cyclodextrin containing carvacrol and linalool, which are characterized for having low aqueous solubility, high photosensitivity, and high volatility. The nanoparticles produced demonstrated insecticidal activity against ***Helicoverpa armigera*** (corn earworm) and ***Tetranychus urticae*** (spider mite). In addition, repellent activity and reduction in oviposition were observed in the mites. They reduced the toxicity by nanoencapsulation and the combination of the monoterpenes (carvacrol and linalool) was more effective than individual encapsulations; the slow liberation of the insecticidal agents can contribute to sustainable agricultural practices.

de Oliveira et al. (2018) used zein NPs as carriers loaded with the essential oil citronella (geraniol and R-citronellal), commonly used as an insect repellent, but they are susceptible to photodegradation and volatilization. The assays of cytotoxicity and phytotoxicity showed that encapsulation of the botanical repellents decreased their toxicity. Repellent activity tests showed that nanoparticles containing the botanical repellents were highly effective against ***Tetranychus urticae*** (Koch mite). Therefore, the challenge is to develop species-specific nanoproducts and verify their potential at field levels.

Gharenaghadeh et al. (2017) developed nanoemulsions containing ***Salvia multicaulis*** essential oil (mostly monoterpene hydrocarbons, 58.01%) and determined that the antimicrobial activity of the essential oil-containing nanoemulsions against foodborne bacteria (***Bacillus cereus***, ***Enterococcus faecalis***, ***Klebsiella pneumoniae***, and ***Moraxella catarrhalis***) was higher than in essential oil-free nanoemulsions. Pasquoto-Stigliani et al. (2017) studied poly(ε-caprolactone) nanocapsules loaded with neem oil and oleic acid, and determined the cyto-, geno-, and phytotoxicity pof the products. It was observed that the soil microbiota was not affected in 300 days (compared to the control) and that net photosynthesis and stomatal conductance of maize plants were not affected by higher oil concentrations (200 mg of neem oil). However, treating with oleic acid mixed with neem oil (100 mg each) showed more toxicity in the same assay. This variability in effect again is a challenge for future product development.

A study by Guerra-Rosas et al. (2017) exhibited the antimicrobial activity of nanoemulsions containing oregano, thyme, lemongrass, or mandarin essential oils with high methoxyl pectin against *Escherichia coli* and *Listeria innocua*. The highest antimicrobial activity detected against *E. coli*, reaching 5.9 log reductions of the population of *E. coli*, was for the treatment with the lemongrass-pectin nanoemulsion. In a recent study, Kumari et al. (2018) formulated a nanoemulsion with thymol and a glycoside surfactant from *Quillaja saponin* to protect against *Xanthomonas axonopodis*, which causes bacterial pustule disease in soybean plants. The nanoemulsion (0.01%–0.06%, v/v) showed substantial in vitro growth inhibition of *X. axonopodis* (6.7–0.0 log CFU/mL) and significantly lowered the disease severity (33.3%–3.3%) in plant seed treatment and foliar application of the nanoemulsion (0.03%–0.06%, v/v). There was an increased efficacy (54.9%–95.4%) in the control of the bacterial pustule in soybeans and a positive growth-promoting effect by the nanoemulsion. Similarly, Wan et al. (2018) showed that there were antifungal and inhibitory activities toward mycotoxin production in two chemotypes of *Fusarium graminearum* when a clove oil-in-water nanoemulsion in effective concentration was applied. They found that these activities were significantly enhanced when the clove nanoemulsion was encapsulated. This points to the effective role the essential oil compounds can play in the future in developing nano-based products for crop protection.

A novel area of development in nanotechnology is nanosensors. At present, very promising nanosensors are being developed for use in the field without the need for a sophisticated laboratory, highly qualified personnel, or expensive equipment that is difficult to operate. Portable nanosensors are expected to be used directly in the field and detection would be in real time to have an efficient diagnosis and achieve better production (Khater et al., 2017). Nanosensors are sensitive and efficient detection tools used to monitor agrochemicals, phytopathogens, soil moisture, soil pH, etc., and can further increase the productivity of different processes (Saxena et al., 2017). There are some recent examples of new developments in this area. A sensitive and straightforward label-free colorimetric detection method using unmodified gold NPs as colorimetric probes was developed to detect the cucumber green mottle mosaic virus at concentrations as low as 30 pg/μL (Wang et al., 2017). Zhao et al. (2014) used Au NP labels through the amplification of the analytical signal. The sensitivity of the immunological assay was much improved, and hence *Pantoea stewartii* subsp. *stewartii* could be detected. Fluorescent silica nanoparticles combined with antibody molecules successfully detected the plant pathogen *Xanthomonas axonopodis* pv. *Vesicatoria*, which causes bacterial spot disease in tomatoes and peppers (Yao et al., 2009). A novel nanosensor was developed by Baetsen-Young et al. (2018) that was made with unamplified genomic DNA (gDNA) to fight against *Pseudoperonospora cubensis* (cucurbit downy mildew). They successfully detected as little as 2.94 fM of pathogen DNA, using crude extractions of a pathogen matrix as low 18 spores/μL.

2.10 Conclusion

This chapter focused on specific applications of nanomaterials in crop protection such as crop growth promotion, nanofertilizers, nanocarriers, and nanodevices, among others. Several remarkable and informative results confirmed the advantages of using nanotechnologies to protect crops and help increase crop yields. However, the need for more research and development in agronanobiotechnology for food security is required in the future. However, some questions have been posed pertaining to their use in agriculture, specifically in terms of their toxicity that can impact human health and the environment; these need to be addressed.

It must be highlighted that the evaluation and application of nanomaterials in agricultural soils could be of tremendous value to abate the current global food scarcity, but such materials could also become potential environmental pollutants. Therefore, toxicity level studies must be evaluated and improved continuously. It is important to bear in mind that specific tests must be carried out for each condition and generalization regarding the effect of engineered nanomaterials on crops, and their impact on human and environmental health should be avoided.

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10.2.4 Artículo 4. La investigación en nanotecnologia llevada a una política pública en México. (En preparación)

LA INVESTIGACIÓN EN NANOTECNOLOGIA LLEVADA A UNA POLITICA PÚBLICA EN MEXICO

Resumen— Las nanotecnologías agrícolas ya están en el mercado, pero no se cuenta con suficiente información sobre su uso, y efectos positivos o negativos; lo anterior debe ser considerado y evaluado toda vez que pueda servir para la creación de políticas públicas que permitan regular su aplicación, distribución y comercialización, sin que ello comprometa la cantidad y calidad de alimentos que produce el sector agrícola mexicano. Con base en un análisis de los componentes económico, social y ambiental de la nanotecnología agrícola se pretende guiar el desarrollo y creación de políticas públicas en México. Se plantean los siguientes objetivos: 1) Establecer el efecto potencial de la nanotecnología agrícola sobre la autosuficiencia alimentaria, el cuidado del ambiente y el bienestar social, 2) Obtener un diagnóstico actualizado sobre los lineamientos e instrumentos de apoyo federal, estatal y municipal para el desarrollo de dichas tecnologías en México y elaborar una propuesta de recomendaciones de lineamientos e instrumentos que fomenten la sustentabilidad de los proyectos y empresas, maximizando el impacto positivo ambiental, económico y social.

Palabras clave— Palabras clave: Nanotecnología, nano ciencia, agricultura, política pública.

Introducción

A nivel mundial la nanotecnología y la nano ciencia han abierto posibilidades en la innovación científica y tecnológica, además han tenido influencia en el ahorro de materiales y la reducción de contaminantes. Esta nueva revolución ha sido bien aceptada en industrias como la farmacéutica, textil, petroquímica, solo por citar algunos casos. Sin embargo, también existen avances en la agricultura y la gestión ambiental, pero son poco difundidos y aplicados. La nanotecnología se puede definir como el diseño, creación, síntesis, manipulación y aplicación de materiales, aparatos y sistemas funcionales a través del control de la materia a escala nanométrica es decir, menor que 100 nm (Dowling et al., 2004). A partir del siglo XXI, la nanotecnología se emplea en prácticamente todas las áreas científicas y tecnológicas alrededor del mundo, mientras que más de 7400 millones de personas demandan alimentos, un medio ambiente limpio y buena calidad de vida. La nano ciencia es el estudio de la materia a nivel del nanómetro, escala en la cual las propiedades físicas y químicas de los sistemas difieren de las de los sistemas macroscópicos, convirtiéndolas en únicas (Dowling et al., 2004). Los términos nanotecnología y nanociencia engloban un conjunto de conocimientos y tecnologías comunes en varias disciplinas científicas tradicionales como la química, física, tecnología, medicina, ciencias biológicas y ciencias ambientales.

La Organización de las Naciones Unidas para la Alimentación y la Agricultura (FAO) publicó en 2013, información sobre el estado del arte de la nanotecnología en alimentos y agricultura, en su reporte documentó investigaciones llevadas a cabo durante 10 años, enfocadas hacia la sostenibilidad y soluciones a los problemas ambientales. Estas investigaciones se centran en: la liberación de ingredientes activos como manejo de enfermedades y protección de cultivos, la pérdida de la fertilización y aumento del rendimiento, así como la producción de bio-nano compuestos de cultivos tradicionales (Parisi *et al*., 2014). Los informes de dichas investigaciones sobre posibles aplicaciones en la agricultura han sido tanto positivos como negativos. Nuestro conocimiento sobre las interacciones de las nanopartículas de uso agrícola con el medio ambiente aun es limitado y debido a la complejidad que representa, todavía hay un largo camino para entenderlo completamente.

La nanotecnología podría suministrar herramientas a la agricultura moderna e incluso ser útil en la solución de los problemas futuros de los alimentos y la demanda energética con un enfoque sostenible.

México tiene un territorio de 198 millones de hectáreas, de los cuales cerca de 30 millones son tierras de cultivo, la agricultura participa con el 3.1% de producto interno bruto (INEGI, 2016) sin embargo, se trata de un sector importante por sus funciones en el desarrollo económico, social y ambiental del país. La agricultura emplea al 13% de la población, y marcando relevancia de uso territorial cerca del 24% de la población vive en zonas rurales, amenazado por ser un sector poblacional que fluctúa y que disminuye por temas de migración, y cambio de uso de suelo. Aunque hablamos de un sector en crecimiento, la agricultura está también fuertemente influenciado por las temporalidades, y sujeto a la oferta y la demanda.

En México, la investigación en nanotecnología aplicada a la agricultura tiene algunas limitantes: a) los materiales de investigación tienen elevados costos; b) se desconoce el procedimiento de obtención de los insumos, c) aún no se cuenta con la instrumentación adecuada, d) faltan evidencias de estudios de toxicidad en campo, e) el marco regulatorio para uso y liberación de nanomateriales en campos agrícolas es nulo; entre otros.

Descripción del Método

Se utilizó la metodología bibliográfica, partiendo de fuentes directas e indirectas, así como fuentes documentales (informes técnicos, artículos científicos, folletos, ponencias entre otros) y fuentes de publicaciones secundarias como reseñas, referencias de revistas y periódicos. Se analiza el contenido temático de un conjunto de documentos científicos en una búsqueda limitada a las palabras nanotecnología, nanociencia, agricultura y México, tomando como referencia el periodo 2000-2017. Para la búsqueda de los documentos en base de datos de artículos científicos y revistas científicas se establecieron las siguientes restricciones: a) área de conocimientos científicos humanísticos; b) presencia en Palabras Claves.

a) Efectos de las nanopartículas en los cultivos de importancia alimentaria

Hoy en día el principal objetivo de la agricultura es incrementar la producción y esto conlleva a la aplicación de diversas estrategias tecnológicas que afectan el crecimiento y, por lo tanto, la fisiología de las plantas cultivadas objeto de interés, teniendo impactos en la calidad de los alimentos vegetales. En este siglo, el uso de nanopartículas ha sido experimentalmente documentado con estudios a favor y en contra. La agro-nanotecnología, que promete la gestión de los recursos naturales a través de nuevas herramientas y plataformas tecnológicas con recursos limitados de tierra y agua (Mishra et al., 2014), puede ser una solución para la alimentación, la sostenibilidad en el proceso de producción y la mejora ambiental. Muchos trabajos en áreas de captación, translocación, acumulación y toxicidad se realizan con diferentes ámbitos para tratar de explicar la interacción entre nanoparticulas y planta para saber la respuesta. López-Moreno et al., 2016, reportaron efectos negativos en la germinación y crecimiento de plantas de tomate (*Solanum lycopersicum L.*), a las que se les expuso a nanopartículas de ferrita de cobalto ($CoFe_2O_4$). Baskar et al., 2015 encontraron que nanoparticulas de plata (AgNP) aplicadas a plántulas de repollo chino (*Brassica rapa ssp. Pekinensis)* a diferentes concentraciones tuvieron un impacto en crecimiento y desarrollo y que a baja concentración actúan como un estimulador del crecimiento y en altas concentraciones retrasa y altera los genes involucrados en glucosinolatos. antocianinas y antioxidantes. Marchiol et al., 2016, reportaron que las nanoparticulas de dióxido de titanio (TiO_2NP) y nanoparticulas de óxido de cerio (CeO_2NP) influyen en el ciclo normal de crecimiento de la cebada (*Hordeum vulgare L.*). Específicamente, los CeO_2NP redujeron la cantidad de macollas, el área foliar y el número de semillas por planta; mientras que los TiO_2NP estimularon el crecimiento de las plantas y contrarrestaron los efectos adversos de los CeO_2NP. Los agregados de TiO_2NPs cristalinos se detectaron en los tejidos de las hojas, mientras que los CeO_2NP no estaban presentes en forma de nanoagregados. Sin embargo, CeO2NP aplicado en dosis alta (500 mg / kg) promovió el desarrollo de la planta con un aumento del 331% en la biomasa aérea en comparación con el control, pero no con los granos formados. Una dosis promedio (250 mg / kg) mejoró la acumulación de Ce en el grano por lo tanto 294% que estuvo acompañada por aumentos en P, K, Ca, Mg, S, Fe, Zn, Cu y Al, así como aumento de metionina, acido aspártico, treonina, tirosina, arginina y ácido linolénico en los granos de hasta 617, 31, 58, 141, 378 y 2.47% respectivamente, en comparación con los otros tratamientos.

Jaberzadeh et al., 2013, reportan la aplicación de óxido de titanio en la cebada (*Hordeum vulgare* L.) encontraron que provocó un incremento en el rendimiento de semilla, mientras que las nanopartículas de dióxido de titanio (0.02%) fue más efectiva para mejorar el rendimiento. El mayor rendimiento de semilla se obtuvo cuando las plantas no estresadas bajo estrés hídrico se trataron con nanopartículas de dióxido de titanio (0,02%) durante la etapa de elongación del tallo.

b) La necesidad de medir los efectos socio-ambientales de la aplicación de nanopartículas y sustentabilidad agrícola

El sistema alimentario actual a nivel mundial no es sustentable y por décadas ha causado daños ambientales, entre ellos las emisiones de gases de efecto invernadero, el uso irracional de agua potable, la contaminación de suelos y mantos acuíferos por el nitrógeno y fósforo, el uso de pesticidas, y otros daños. Sin embargo, las investigaciones recientes en materia de nanotecnología ambiental demuestran que esta puede también ser una herramienta útil para reducir la contaminación del medio ambiente. Peters et al. (2016), desarrollaron nanoencapsulados y nanocompuestos para alimentos y aditivos para piensos, biocidas, plaguicidas y materiales en contacto con alimentos.

Ibrahim et al. (2016), aplicaron nanomateriales como catalizadores en procesos de fitoremediación y el uso de estabilizadores para mejorar su rendimiento. La nanotecnología también ofrece alternativas para la recuperación de agua y suelos, ejemplos del uso de nanoproductos en ciencias ambientales son los reportados por Ali et al. (2016), quienes aplicaron nanomateriales para la degradación fotocatalítica de contaminantes orgánicos; Scognamiglio et al., (2016), emplearon nanosensores. Elango y Roopan (2016), usaron nanomateriales para la degradación del azul de metileno; Begum et al. (2016) emplearon nanosensores para la detección rápida de estímulos ambientales como pH, fuerza de iones y moléculas biológicas; Pereira et al. (2015), utilizaron microorganismos para biosíntetizan nanopartículas metálicas y Bogdan et al. (2015), crearon nanomateriales con superficies autodesinfectantes.

La agricultura sustentable se entiende como aquel sistema productivo que logra mantener su productividad y seguir siendo útil a la sociedad a través del tiempo, de modo que se preserven adecuadamente los recursos sin que ello comprometa la alimentación y calidad de vida de generaciones futura; cuando se establecen nuevas tecnologías de cultivo y aun si se trata de las tecnologías convencionales es necesario medir los efectos que esta puede ejercer sobre la sociedad ya sea desde un enfoque económico, social o ambiental.

c) Planteamiento metodológico

La sustentabilidad agrícola puede medirse a partir de índices compuestos que combinan diversos indicadores (Altieri & Nicholls, 2012; 2002). El planteamiento de que índices pueden incluirse en cada caso será a partir del tipo de cultivo (cobertura del suelo, cantidad de materia orgánica, incidencia de plagas, entre otros), a medida que se integran mediciones de subíndices confiables, con repetividad y representativos estas medidas clasificadas como subjetivas se transforman en herramientas útiles para el diseño de políticas públicas, y decisiones de gobierno, pudiendo enriquecerse con los conocimientos de los agricultores. Para la medición de la sustentabilidad agrícola se requiere:

(i) caracterización de los sistemas productivos,

(ii) construcción del marco de análisis sobre sustentabilidad,

(iii) priorización de aspectos para la sustentabilidad,

(iv) definición y estandarización de indicadores,

(v) evaluación de la sustentabilidad,

(vi) análisis de resultados y diagramación, y

(vii) planeación de acciones de mejora.

d) Investigación en nanotecnología agrícola

El caso de la aplicación de la nanotecnología en diferentes sectores productivos supone el mismo problema y en particular las nanopartículas, dado que se trata compuestos actualmente utilizado por la industria. González y Torres 2014, proponen que la sustentabilidad agrícola depende de factores como las técnicas de cultivo, los componentes de dichas técnicas que pueden ser sociales, naturales y económicos.

Se debe dar la nanotecnología en relación con la producción agrícola, como un conocimiento científico y tecnológico transdisciplinario que emerge y que impacte en la dinámica social y económica del país.

Se utiliza la metodología ambiental Presión-Estado-Respuesta, modelo ampliamente conocido para el desarrollo de indicadores ambientales, lo que en su mayoría son datos técnicos con lo que permitirá observar la relación entre ambiente y sociedad (figura 1)

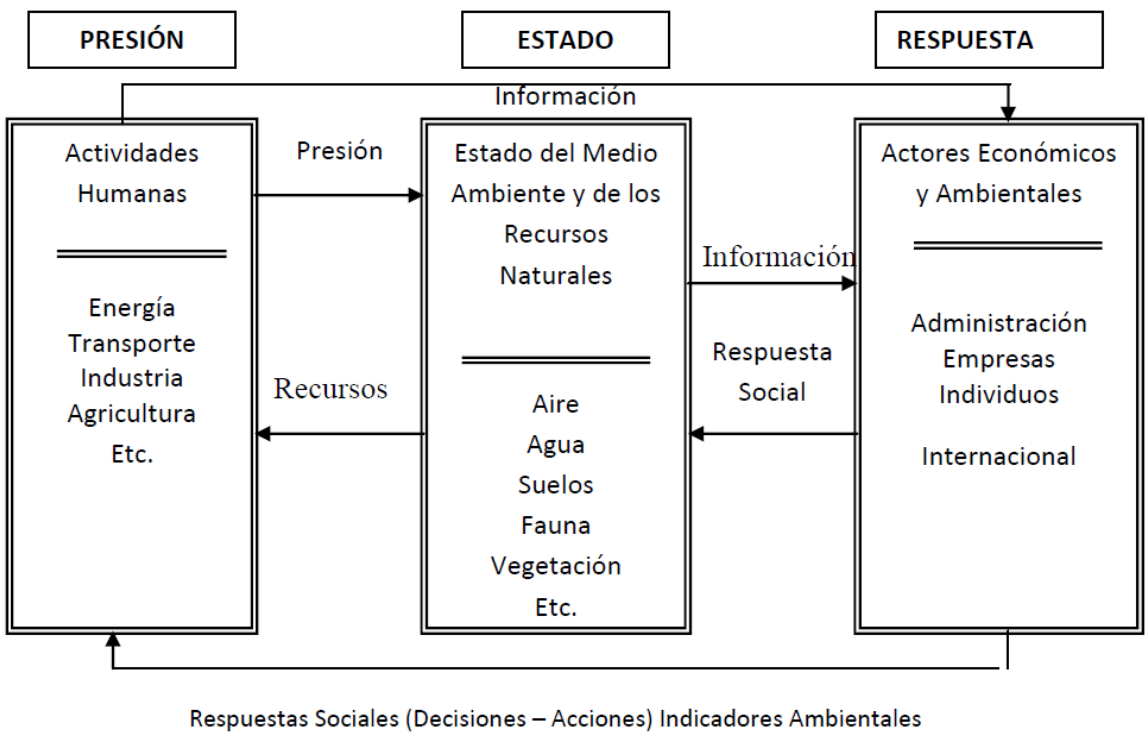

Figura 1. Esquema del Modelo Presión – Estado – Respuesta. (OCDE, 1993, EPA, 1996).

Para poder obtener los datos necesarios para la construcción de indicadores que permitan medir el impacto socio ambiental, se requiere de obtener datos obtenidos experimentalmente, y publicados en revistas JCR.

e) Investigación socioeconómica.

La inclusión de productos de dimensiones nanométricas en el mercado de agroquímicos e insumos agrícolas es una realidad que genera incertidumbre y preocupación sobre el potencial daño al medio ambiente y a la salud pública, aún a pesar de que algunos nanomateriales sí incrementan significativamente el crecimiento y desarrollo de los cultivos, así como sus componentes de rendimiento. Es necesario documentar y evaluar las aplicaciones nanotecnológicas que se están comercializando en el sector agrícola mexicano, a fin de contribuir con el avance tecnológico.

El interés de las empresas y del Estado en la nanotecnología agrícola está limitado por la incertidumbre ante los efectos aún desconocidos en este caso, toda vez que se trata de la producción de alimentos, una vía rápida para consumir nanomateriales. Se debe presentar un panorama real de la nanotecnología aplicada a la agricultura, mostrándola como una herramienta útil en la búsqueda de la sustentabilidad, si las evidencias así lo permiten. Los nanomateriales podrían incrementar significativamente los rendimientos y la calidad de los alimentos, ligado a otros beneficios en materia de retorno de inversión, pero, las consideraciones ambientales, sociales y económicas deben ser tomadas en cuenta, y analizadas proporcionan un panorama real sobre su aplicación.

Los siguientes son los lineamientos específicos que se pueden establecer en las políticas públicas para ser desarrollados por la agenda de gobierno y los agentes interesados:

- Bases metodológicas para evaluar el efecto económico, social y ambiental de la nanotecnología agrícola en México

- Analizar las características económicas, sociales y ambientales de la nanotecnología agrícola en países en los que existe un presupuesto de investigación y aplicación.
- Evaluar con base en la aplicación de la metodología diseñada, el impacto económico, social y ambiental de la nanotecnología en zonas geográficas de posible influencia en México.
- Conocer y analizar las características de las de empresas fabricantes de fertilizantes y plaguicidas en las que se busque aplicar o se haya aplicado la tecnología nano; y tipificarlas de acuerdo con un modelo de indicadores de desempeño y factores de éxito, así como estimar el costo-beneficio del desarrollo de la nanotecnología agrícola, a partir de determinar el nivel de beneficios resultantes del gasto de inversión.
- Obtener un diagnóstico actualizado sobre los lineamientos e instrumentos de apoyo federal, estatal y municipal para el desarrollo de dichas tecnologías en México y elaborar una propuesta de recomendaciones de lineamientos e instrumentos que fomenten la sustentabilidad de los proyectos y empresas, maximizando el impacto positivo ambiental, económico y social.

En México la nanotecnología es incipiente, como lo marca Foladori (2011:4):

> …la presencia de las nanotecnologías creció y se extendió por toda América Latina durante la primera década del siglo XXI. Políticas de ciencia y tecnología han desempeñado un papel importante en el desempeño de estas nuevas tecnologías. Diversas instituciones internacionales, como el Banco

> Mundial, la organización para la cooperación económica y desarrollo y la organización de Estados Americanos promovieron políticas similares de ciencia y tecnología e incluyeron la nanotecnología como un área prioritaria

Como lo menciona Aguilar Villanueva (1996:16), en su libro de "La Hechura de las políticas":

> Lindblom en su método de análisis para las decisiones de gobierno se desplazó hacia una propuesta "incremental", gradual, de gobernar y hacer política (incremental politics), aumenta correctivamente vez por vez el margen de maniobra de un gobierno…

Reitera:

> Lindblom quiere decir que los problemas, necesidades y conflictos, que inevitablemente aparecen en la vida social, encuentran su planteamiento y desahogo gracias a los inteligentes entendimientos, arreglos y transacciones de los actores sociales; considera entonces que los ciudadanos resuelven con mayor frecuencia sus problemas a través de libres competiciones y cooperaciones, más que a través de una sistemática intervención fiscal y regulatoria del estado.

En el Plan Nacional de Desarrollo 2013-2018 (2013:44) expresa claramente la situación de México:

> De acuerdo con estimaciones del CONEVAL, 28 millones de personas no

> tuvieron acceso a una alimentación adecuada en 2010. De éstos, 7.4 millones se encuentran en pobreza extrema.

El hambre es la expresión más lacerante de la pobreza extrema. Cuando afecta a los niños pequeños genera daños físicos e intelectuales irreversibles que los condenan a repetir el mismo ciclo de pobreza que sufrieron sus padres. De acuerdo con la Encuesta Nacional de Salud y Nutrición (ENSANUT), en 2012, 2.8% de los menores de cinco años presentan bajo peso, 13.6% muestran baja talla, 1.6% desnutrición aguda (emaciación) y 23.3% anemia.

La falta de acceso a los alimentos se agrava con la pérdida del poder adquisitivo de los hogares. De acuerdo con el CONEVAL, entre 2008 y 2010, en un escenario de crisis económica y volatilidad de precios internacionales de alimentos, la única carencia social que aumentó su incidencia fue la alimentaria. Hasta antes de abril de 2010, el crecimiento del valor de la canasta alimentaria fue mayor que el de la inflación promedio, cuestión que afecta en mayor medida a las personas de menores ingresos (debido a que destinan una proporción más elevada de su gasto a la compra de alimentos). Dicha dinámica se debió, en parte, a factores externos. Por ejemplo, en los últimos años, el aumento del consumo per cápita de todos los alimentos de China ha impactado significativamente la demanda de los mismos y se ha traducido en un incremento de sus precios a nivel mundial.

Por otro lado, la distribución del ingreso del país representa un reto para el desarrollo nacional y la equidad social. En la última década, México fue la segunda nación más desigual de la Organización para la Cooperación y el Desarrollo Económicos (OCDE) después de Chile y la doceava en América Latina, de acuerdo con cifras de la Comisión

Económica para América Latina y el Caribe (CEPAL). Con datos de la Encuesta Nacional de Ingresos y Gastos de los Hogares (ENIGH) 2010, se observa que la relación de ingresos entre el 10% de la población más rica y el 10% más pobre fue de 25 a 1. En términos de desigualdad, también destaca que el 44% de la clase trabajadora del país percibe ingresos por debajo de dos salarios mínimos mensuales, a 2010 el 31.8% de los mexicanos no contaba con acceso a algún esquema de salud y 60.7% de la población no tenía seguridad social (Plan Nacional de Desarrollo, 2013:44)

f) Actores que intervienen en la política pública en nanotecnología.

Para la elaboración de la Política pública debemos comprender tres aspectos materiales: los actores que intervienen, la temporalidad y la espacialidad.

Mientras que de los agentes hablaremos de 3:

a. La sociedad en donde los centros de investigación y educativos, las asociaciones civiles, sociedades todas ellas sobre nanotecnología y agricultura.

b. El gobierno que regula la nanotecnología y la agricultura.

c. La iniciativa privada a través de las cámaras de comercio, las empresas que ven en la nanotecnología materia para sus negocios, así como las empresas agrícolas.

De acuerdo a Foladori y Zayago, (2010), en México no existe discusión sobre los impactos sociales, legales, laborales y sobre el medio ambiente y la salud de la nanotecnología. El diseño de los programas en CYT recae sobre las empresas, el gobierno y la academia. Hay otros actores sociales que también deben de participar en el diseño de la política tecnológica y en un plan nacional de nanotecnología, pues son estos actores los que han influido en la trayectoria de desarrollo de la nanotecnología a nivel mundial, por lo que la identificación de estos agentes debe ser específica a problemas y grupos sociales.

- Evaluación del status tecnológico en el campo de la nanotecnología Agrícola hasta ahora desconocido en México.
- Plantear posibles aportaciones útiles en el campo de regulación de desarrollo y aplicación de las nanopartículas de importancia agrícola, como guía para la elaboración de políticas públicas.
- Análisis del desarrollo impulsado por la investigación científica a nivel nacional e internacional de las tecnologías de innovación en la aplicación de nano materiales de importancia agrícola.
- Aprovechamiento, usos e impactos ambientales de la nanotecnología en la agricultura, y en los indicadores de sustentabilidad.

Si bien como hemos podido ver en el presente documento, la nanotecnología es incipiente en México, por lo que los actores en la política se van acomodando a la realidad nacional, pero sin embargo podemos definir tres grupos de actores que participan en tal forma en nanotecnología y alimentos:

Grupo I. Perteneciente a órganos del estado: CONACYT, Poder Ejecutivo (secretarías correspondientes como SEMARNAT, Secretaría de Economía), Poder Legislativo (Comisión de ciencia y Tecnología).

Grupo II. Perteneciente a instituciones sociales (educativas, asociaciones civiles, sociedades civiles entre otros): CINVESTAV, IPN Centro de Nanociencias y Micro Nanotecnologias, Centro Virtual Brasil México, Centro de Investigaciones en Óptica en A.C. (CIO), Laboratorio Nacional de Nanotecnología (CIMAV-NANOTECH), Mundo Nano, Centro de Nanociencias y Nanotecnología de la UNAM, Red de Grupos de Investigación en Nanociencia, UAM Iztapalapa, Centro de Investigación en Alimentos y Desarrollo, Red Latinoamericana de Nanotecnología y Sociedad, Programa de Ganadería del Colegio de Postgraduados, Programa de Edafología del Colegio de Postgraduados.

Grupo III. Perteneciente a particulares: TecNM, entre otras.

Zayago (2011:329-330) menciona que la relevancia para los más desprotegidos. El objetivo de la plataforma científico- tecnológica de México ha cambiado en los sexenios; pasó de priorizar las necesidades en salud, agricultura e industria a responder a las necesidades del mercado y la competitividad del sector privado; como ya lo hemos visto anteriormente del presente documento.

En cuanto a la temporalidad diremos que se observara la política del último Plan Nacional de Desarrollo, es decir, PND 2013 al 2018. Y como espacio de estudio la parte territorial será la República Mexicana, qué es donde conviene por las escazas instituciones que existen específicamente en la parte agroalimentaria y la nanotecnología.

g) Regulación de la nanotecnología en el uso agrícola.

De acuerdo a los Lineamientos para regulaciones sobre nanotecnologías para impulsar la competitividad y proteger al medio ambiente, la salud y la seguridad de los consumidores[1], expresa que:

En el l artículo 4o de la Constitución Política de los Estados Unidos Mexicanos, el Estado Mexicano tiene como responsabilidad garantizar los derechos de las personas a la protección de la salud y a un medio ambiente sano, así los reglamentos y las leyes específicas correspondientes que contienen disposiciones aplicables son las siguientes:

- La Ley General de Salud
- Ley General para la Prevención y Gestión Integral de Residuos, artículo 1
- Ley Federal de Trabajo, art. 3º y en la Ley General de Salud Capítulo V
- Ley Federal de Sanidad vegetal, art. 1º
- Ley de Caminos, Puentes y Autotransporte Federal, Art. 50

Mientras que la Ley Federal sobre Metrología y Normalización, en su artículo 40, dispone que los reglamentos técnicos (NOM) deben establecer:

a. Las características y/o especificaciones que deban reunir los productos y procesos cuando éstos puedan constituir un riesgo para la seguridad de las personas o dañar la salud humana, animal, vegetal, el medio ambiente general y laboral, o para la preservación de recursos naturales; y,

[1] http://www.fan.org.ar/wp-content/uploads/2014/05/lineamientos-regulaciones-nanotecnologias-Mexico.pdf

b. La determinación de la información comercial, sanitaria, ecológica, de calidad, seguridad e higiene y requisitos que deben cumplir las etiquetas, envases, embalaje y la publicidad de los productos y servicios para dar información al consumidor o usuario.

Un cambio radical al anterior Programa Especial de Ciencia, tecnología e innovación 2008-2012, que indicaba más la parte de nanotecnología y la describe:

Las prioridades del sector CTI deben incluir temas relevantes de la agenda internacional como relevantes de fuerte dinámica y atención prioritaria son la biotecnología, la nanotecnología y los materiales (PECITI, 2008:16).

Sin embargo, en el actual Programa Especial de Ciencia y Tecnología 2014-2018 tiene como tema prioritario en desarrollo Tecnológico el Desarrollo de nanomateriales y de nanotecnología (PECITI, 2014:51) y no menciona de qué forma o en qué sentido dirigir esos temas; mientras que en el mismo programa en el Área sociedad habla de Combate a la pobreza y seguridad alimentaria (Zayago, 2011:320-321), esto es que aun cuando el mismo programa no vincula, si tienen referencia de ser temas prioritarios.

Si bien las bases del presente tema tienen la nanotecnología en alimentos para subsanar la deficiencia alimentaria, responde muchas de las situaciones que se deben tratar en la política pública iniciando por la agenda de gobierno.

Un acercamiento a la política pública para la nanotecnología agrícola.

De acuerdo a Zayago (2011:320-321) la política mexicana en ciencia y tecnología CyT se ha intentado coordinar con el sector empresarial, aunque los esquemas han variado en cada sexenio. El Estado intentó vincular la CyT con la producción y el consumo en un principio, pero en los últimos años éste ha compartido la responsabilidad con empresas, universidades y centros de investigación, y ha utilizado al mercado para transferir a la sociedad los posibles beneficios tecnológicos

El Plan Nacional de Desarrollo 2012-2018 en su página 9 explica las estrategias para lograr un México Incluyente, en el que se enfrente y supere el hambre. Delinea las acciones a emprender para revertir la pobreza. Muestra, también, el camino para lograr una sociedad con igualdad de género y sin exclusiones, donde se vele por el bienestar de las personas con discapacidad, los indígenas, los niños y los adultos mayores.

En México no existe discusión sobre los impactos sociales, legales, laborales y sobre el medio ambiente y la salud de la nanotecnología. El diseño de los programas en CyT recae sobre las empresas, el gobierno y la academia. Hay otros actores sociales que también deben de participar en el diseño de la política tecnológica y en un plan nacional de nanotecnología, pues son estos actores los que han influido en la trayectoria de desarrollo de la nanotecnología a nivel mundial (Foladori y Zayago, 2010).

El papel de la CyT en el desarrollo de México ha cambiado a partir de las diferentes visiones del gobierno. La política científica actual, que está vinculada al sector privado y al mercado, moldea el desarrollo de la CyT en México.

El Doctor Luis F. Aguilar (1993b, 1 y ss), en su artículo “Problemas Públicos y Agenda de Gobierno”, establece que una de las dificultades en primer lugar se debe definir el problema y señalar los problemas que prioritariamente son públicos, ya que en su estudio señala que existen otros temas que suelen ser confundidos como públicos, por lo que deben ser seleccionados, para ser atendidos por el gobierno y ser incluidos en la atención de la agenda de gobierno.

El desarrollo de una política pública, comienza desde su implementación, pues la manera en que se estudia tiene diferentes niveles y la forma en que se aborda, por lo que conviene establecer las faces que la caracterizan, para determinar las etapas que debe seguir su implementación e inclusión en la agenda de gobierno, sin embargo si no se establecen las condiciones científicas en el análisis de nanotecnología primero, segundo un estudio socio económico, y un estudio socio ambiental como tercer punto, no se puede iniciar el establecimiento de políticas y mucho menos de políticas públicas.

Considerando a Meny y Thoening (1992:105), establecen que una política pública se compone de cinco fases: "a) identificación de un problema: el sistema político advierte que un problema exige un tratamiento y lo incluye en la agenda de una autoridad pública; b) la formulación de soluciones: se estudian las respuestas, se elaboran y se negocian para establecer un proceso de acción por la autoridad pública; c) la toma de decisiones: el decisor público oficialmente habilitado elige una solución particular que convierte en política legítima; d) la ejecución del programa: una política es aplicada y administrada sobre el terreno. Es la fase ejecutiva; y, e) la determinación de la acción: se produce una evaluación de resultados que desemboca en el final de la acción emprendida".

Para efectos de la nanotecnología conviene tomar los pasos que son tratados por el autor Trinidad Zaldívar (2006 y ss.), basados en Eugene Bardach en su obra "Los ocho pasos para el análisis de Políticas Públicas" ya que en la implementación de la creación de una política pública en materia de nanotecnología, hay elementos que han expuesto los autores y que no aplican al caso en concreto, por lo que para efecto de comprender la necesidad de la creación de un plan de acción en esta materia como una prioridad para dar solución a la problemática existente. Así mismo, conviene proponer las siguientes fases: 1. Definición del Problema, 2. Incorporación de la agenda, 3. Construcción de alternativas, 4. Decisión; 5. Implementación, 6. Análisis, 7. Evaluación de resultados, y 8. Resultados del impacto de la política pública en nanotecnología agrícola.

Conclusiones.

La nanotecnología es incipiente en México por lo que se deben establecer condiciones en Política Pública para la regulación de la aplicación y uso en productos agrícolas

Los 3 agentes participantes deben establecer las condiciones para trabajar a la par y subsanar la deficiencia agroalimentaria en medida que los trabajos en nanotecnología lo permitan.

La política pública es relación a la nanotecnología en el uso agroalimentario es de política incremental.

Debido a la tecnología incipiente en nanotecnología existen pocas instituciones que trabajen directamente en regiones específicas por lo que se debe acudir o analizar desde el punto de vista nacional.

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Legislación.

Constitución Política de los Estados Unidos Mexicanos

Ley General de Salud

Ley General para la Prevención y Gestión Integral de Residuos

Ley Federal de Trabajo

Ley General de Salud

Ley Federal de Sanidad vegetal

Ley de Caminos, Puentes y Autotransporte Federal

Ley Federal sobre Metrología y Normalización

Lineamientos para regulaciones sobre nanotecnologías para impulsar la competitividad y proteger al medio ambiente, la salud y la seguridad de los consumidores. Extraído de: http://www.fan.org.ar/wp-content/uploads/2014/05/lineamientos-regulaciones-nanotecnologias-Mexico.pdf

10.2.5 Artículo 5. A view into the research focused on agricultural nanotechnology: Scientific collaboration and community structure. (En preparación para la revista Scientometrics de Springer).

A view into the research focused on agricultural nanotechnology: Scientific collaboration and community structure

Abstract

For almost twenty years, nanoscience research is producing nanotechnology applications that promises to generate advances and benefits for society, today it offers improvements in several industry sectors; medicine, energy, food, transportation among others. One of the important areas is agricultural production. The objective of this study is to investigate global scientific collaboration in agricultural nanotechnology. This study was conducted as a way to explore the flow and the complexity of scientific collaboration networks and its impact on the number of global publications on agricultural nanotechnology the data presented refer to the period 2000-2018. The information was retrieved from the Web of Science database using the strategy of temporal delimitation: it recovers for long periods of time (2000-2018), thematic delimitation: "nanotechnology and agriculture". The criteria of selection of the scientific production generated in the form of articles and book chapters, under this search parameter; 1010 records were recovered in total. The modularity class value was 0.96 that score, and it indicates a community structure, and it describes how the network is divided into sub-networks. There were 3314 related components; this value shows a high connection inside the sub-networks, 80.90% of the nodes.

Keywords. Scientific collaboration, nanotechnology, agriculture, global

Introduction

The study of scientific collaboration networks gives a wide view of science advance and let us know how the knowledge flow in a specific field of study. The formation and fortification of the scientific collaboration networks reduces the gap of knowledge inequality between countries and within countries, between provinces or districts. Researchers not only share information, they also share, for example, intellectual or economic resources (Vanz, 2010).

The analysis of social networks follows a methodology based on the analysis of the configuration of the relationships that are formed in a system, elaborating maps, matrices and graphs, additionally include qualitative type analysis or quantification (Wasserman and Faust, 1994). Scientific cooperation has been addressed in other studies (Newman, 2004; Glänzel & Schubert, 2004) and the production of scientific knowledge has been carried out (Sandstrom et al. 2000). These studies position the scientific publications as a source of information on how science develops within research groups, field of knowledge or geographic region (OECD 1997). In the case of nanotechnology, several studies have been carried out with the objective to understand how scientific knowledge has developed and how it impacts social spheres (Nie et al, 2009; Hullmann A, 2008; Calero, et al 2006; Fisher, E., & Mahajan, R. L. 2006).

Previously, analysis of the scientific production has been carried out, one is at the level of the documents themselves, through a classification, (Landauer, Laham and Derr, 2004) another way is to represent it using a complex network, where different types of nodes and different types of links are present, this can be a simple way to detect the self-organization of science and the emergence of a new field or the insertion of new categories. However, these representations are complex, and it is necessary to analyze them carefully since they can have a large number of nodes and links. The "community structure" (Roswall & Bergstrom, 2008), consists of dividing the network into groups so that most of the links are concentrated within the groups, although there are only few links between nodes in different groups. This work has the general purpose of analyzing scientific collaboration in nanotechnology with a particular focus on global research in agriculture into the period of 2000-2018.

Nanotechnology is an area of multidisciplinary scientific research that basically works in the design, characterization, manufacture and application of structures created by the manipulation of size and controlled form at nanometer scale (less than 100 nm) that produce complex systems in which they are modified Some specific characteristics (Bawa et al., 2005). Due to the above, a great number of applications have been developed, among them, for example, Medicine, genetics, pharmaceuticals, and agriculture. The FAO public in 2013, information on the state of the art of nanotechnology in food and agriculture, in its report documented research carried out over 10 years, focused on sustainability and solutions to environmental problems. These investigations focus on releasing active ingredients (disease management and crop protection), minimizing the loss of fertilization and increasing yield as well as producing bio-nano compounds from traditional crops (Parisi et al., 2014). Reports of such research on possible applications in agriculture have been both positive and negative. However, there have been reports that favorable results have been found, for example, in the case of fertilization, germination and growth promoters, contamination sensors and other substances and recovery and soil and water treatment (Han 2007). The UN in 2013 raised the need to increase food production, as by 2050 it is estimated that there will be a population of 9.9 million people. There is currently a trend towards the production of energy crops, derived from efforts to mitigate climate change on the one hand, and on the other by the imminent reduction of hydrocarbon reserves.

Methodological procedures

To analyze the scientific collaboration in agricultural nanotechnology bibliometric indicators were used, additionally it was done an analysis of social networking. The Bibliometric indicators were used to describe, monitor, and evaluate activities in science and technology (Gaulthier, 1998). The collaboration network analysis was done using Gephi, it is a software to "import, export, manipulate, analyse, filter, represent, detect communities and export large graphs and networks" (Grandjean, 2015). The matrix for the creation of the co-authoring network the names of the authors and years are in the cells of an Excel spreadsheet, separated by some specific character, like "point and comma".

Information sources

For the search, retrieval and analysis of records in the Web of Science database we used the strategy of: temporal delimitation: it recovers for long periods of time (2000-2018), thematic delimitation: "nanotechnology and agriculture". The criterion of selection of the scientific production generated in the form of articles and book chapters. In this way, 142 records were recovered in total.

The organization of records extracted from the database mainly the field of authors in Microsoft Excel: were separated into pre-established blocks, each set of authors was separated by "point and comma", to obtain a list with the names of the authors of each record. The information of the authors collected and used in this study was extracted from the database between the months of december 2018-junio 2019). The variables established for the search were: institution of the authors; number of articles and knowledge area. The WOS Portal was the source of data related to the geographical origin of articles published in collaboration between international institutions.

Once the search was done, the duplicate results were eliminated and the data was loaded into tables, to determine the frequency of collaboration between the filtered authors. This data analysis mainly included bibliometry and social network analysis. It should be taken into account that the matrices present the frequency of co-authorship between institutions.

Profile of scientific collaboration

To find the aspects related to the scientific impact on the subject of nanotechnology and agriculture, the scientific production was recovered in the 2000-2018 period of the Web of Science database. The selection criteria were in the form of articles and book chapters. With this delimitation 1010 records were recovered. Pajek software was used to represent co-author collaboration and community shaping (this software has developed a leadership as a tool for the development of science networks, over time it has evolved (Networks / Pajek, 2018), with the field of authors a matrix was organized with the records extracted from the database mainly the author field in Microsoft Excel: they were separated into pre-established blocks, each set of authors was separated by “semicolon”, to obtain a list with the names of the authors of each registry for the creation of the co-author network the names of the authors. To describe the structure of the network it was used the Leuven algorithm. It is even more important to achieve a hierarchy of small communities within a network of large dimensions, the information provided provides organizational information and its functionality that in turn provides more knowledge in the case of social networks of scientific collaboration can offer many possible actions, including collaboration plans, recommendations and adaptations of the user interface. The Leuven algorithm operates quickly on extremely large weighted graphs. For each node i, the algorithm calculates the gain in the weighted modularity when it is placed in the community of its neighboring node and then chooses the community that offers the maximum gain. At the end of this first cycle, the algorithm generates the first partition scheme and then repeats the same step while taking into account the grouped communities as new nodes. The algorithm stops once additional increases in modularity are no longer possible. This method has been used to process very large social networks extracted from telephone companies, for example, with more than 2.6 million users (Blondel et al, 2008) For the visualization of the collaboration at the country level in this topic, a matrix was formed with the countries of ascription of the scientific production organized separately (by “semicolon”) by pre-established blocks, each country was assigned its coordinate geographic, for its representation the Geographic Information System QGIS (QGIS, 2018) was used.

RESULTS AND DISCUSSION

Profile of scientific collaboration of global research in agricultural nanotechnology.

It was found that the global network of scientific collaboration in agricultural nanotechnology was composed of 992 co-authors, working at institutions throughout the world. Within the 2000–2018 period, the scientific production of the researchers enrolled in the field of agricultural nanotechnology increased considerably between 2000 and 2018. (Figure 1) These data show the relevance and dynamism of agricultural nanotechnology research during the last two years.

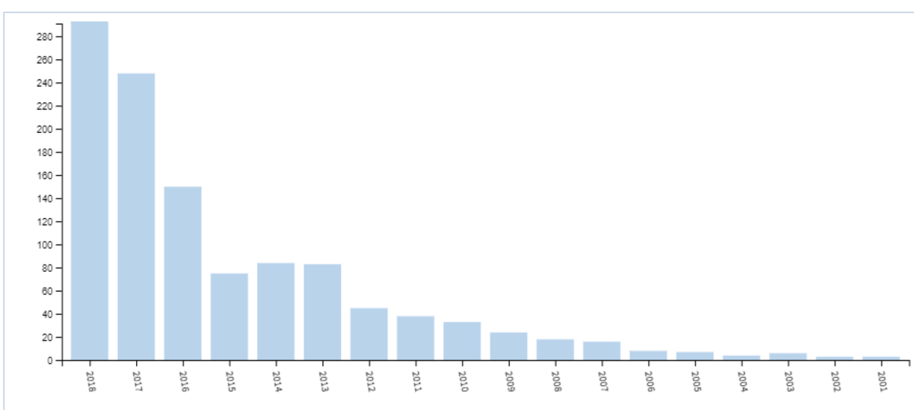


Figure 1. Evolution of the global scientific production of the authors in agricultural nanotechnology research (2000-2018). (Source: Web of Science)

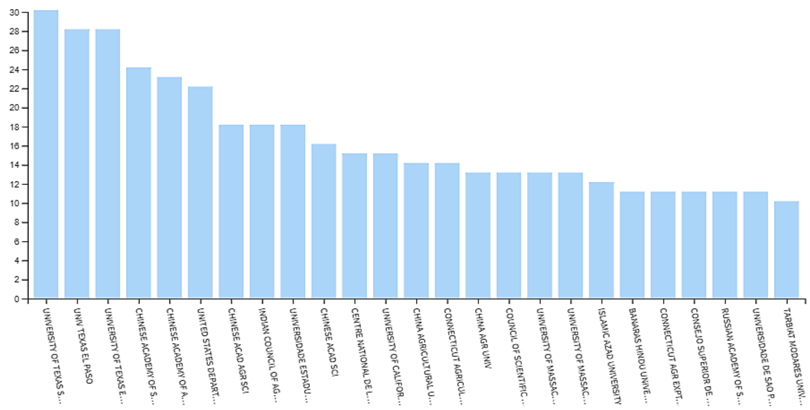


Figure 2. Institutions of affiliation of the authors of documents (articles, reviews and books) during the period 2000-2018. (Source: Web of Science)

The most indexed type of document was the article with 97.003%. The preferred language of publication was English with 97.45%. The Institutions with more indexed documents was the 'University of Texas with 89 documents (8.08%). The Journal of Agricultural and Food Chemistry journal had the highest number of documents (4.905%). Most of the articles were published in journals with an impact factor of 0.5-3.0.

It is observed that the network is integrated by groups of different dimensions interconnected strongly within themselves but with little relation between them. What is described above may be influenced by geographic distance, possibly hindering the relationship, and evidence of the abundance of small sub-groups (Figure 3a). The metrics of the network that were obtained are shown below in table one.

Table 1. Descriptive metrics for the analysed collaboration networks.

Metrics	Values 2000-2018
Average grade	1.47
Network diameter	4
Graph density	0.000
Number of clusters	202
Clustering coefficient	0.98
Related components	3314

Analysing the subgroups that can be observed, there are a complex, non-directed, fragmented network. It is considered a network with very low connectivity between sub-groups with 3314 related nodes, representing 80.90 of total nodes. 95.72% are small subgroups, with 202 clusters which are strongly interconnected, and this is probably because they are geographically isolated. These are small networks of co-authoring, with asynchronous relations, being detected that there are very diverse research subjects that focus the interests of different groups of researchers.

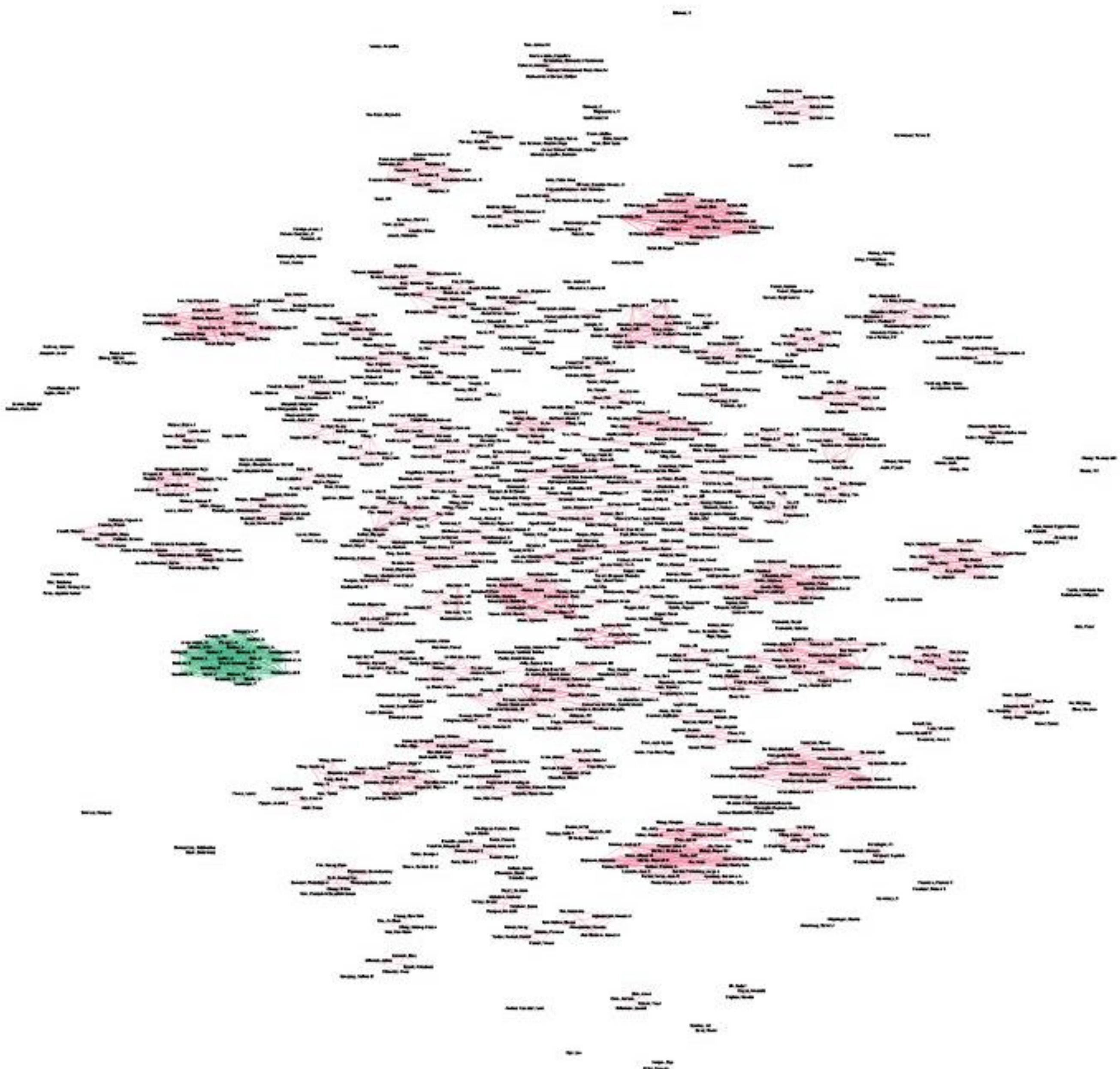
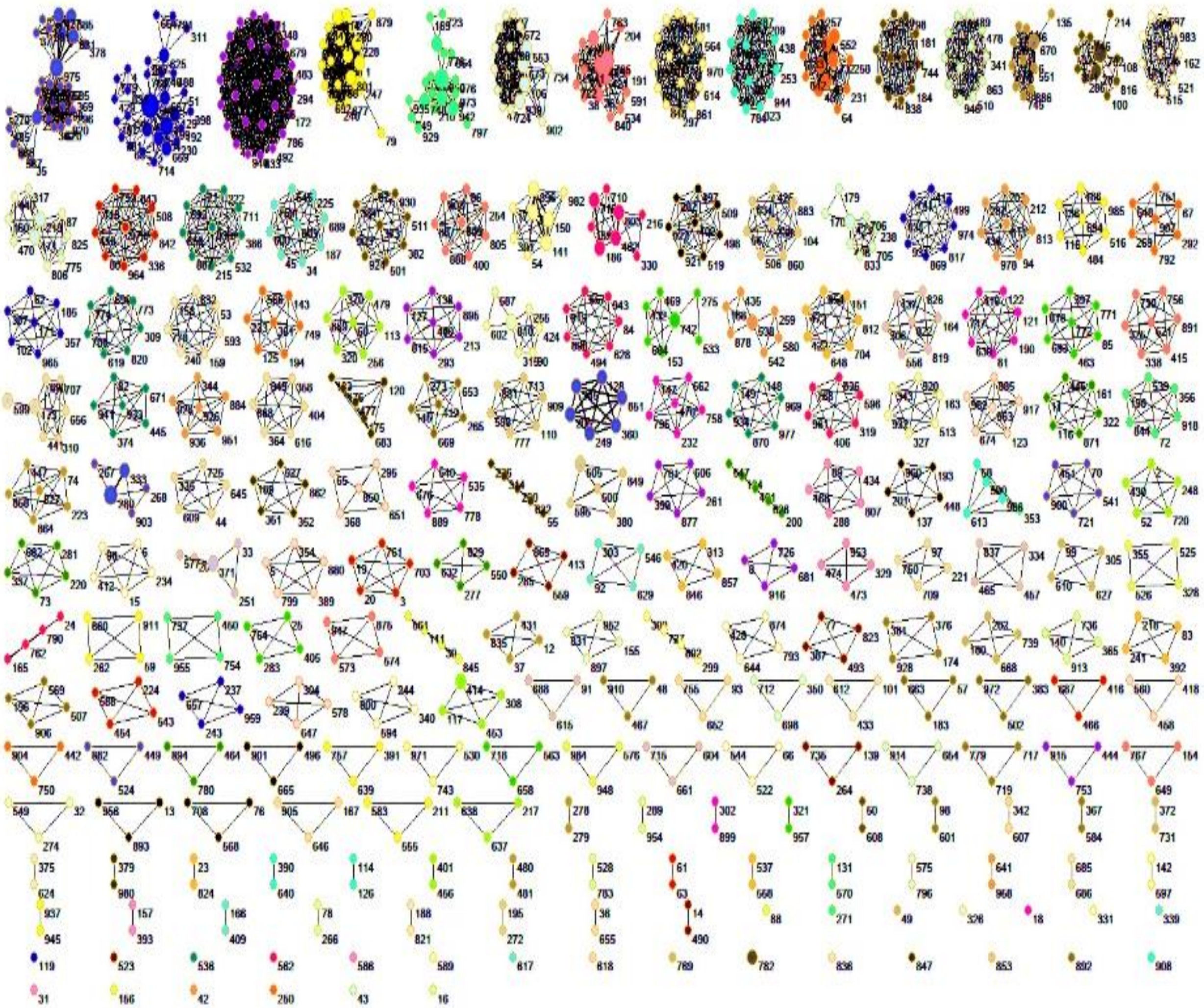
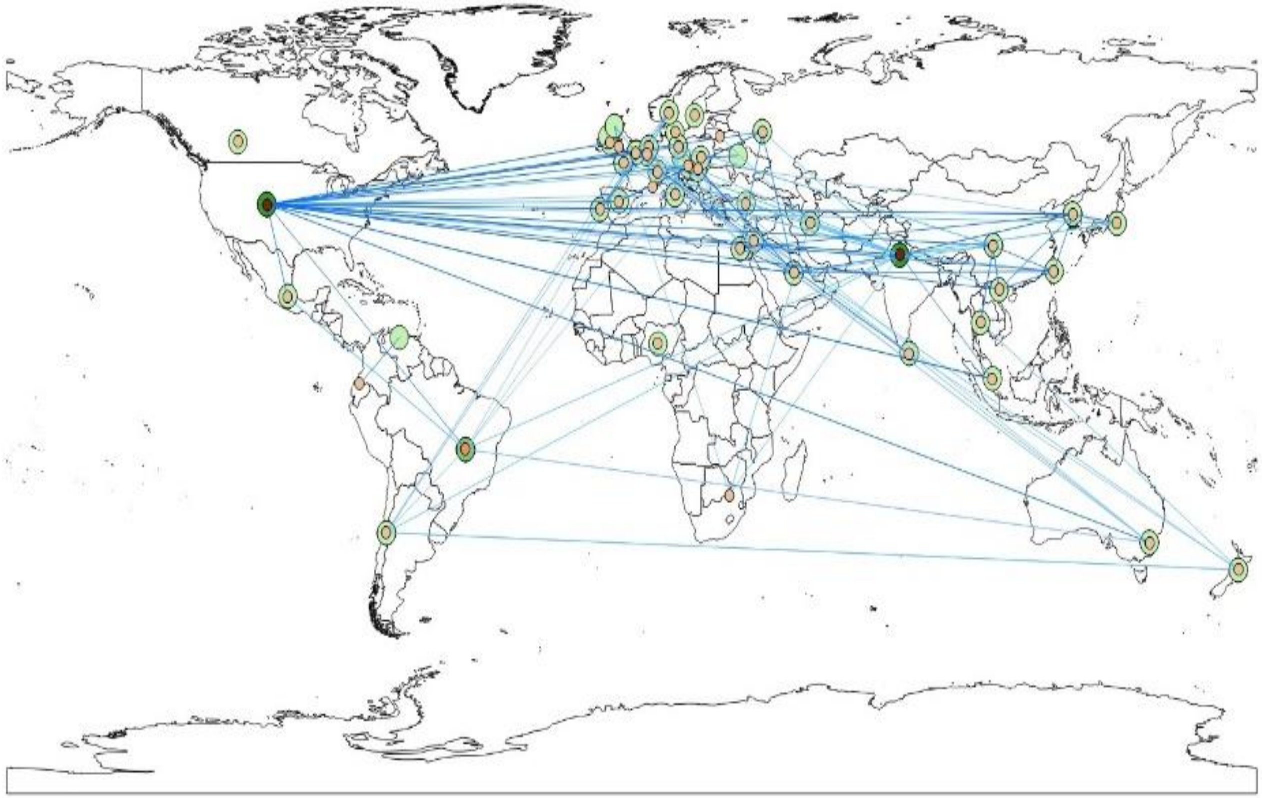


Figure 3(a). Figure 1. General initial graph of the network of scientific research collaboration in agricultural nanotechnology, elaborated with Gephi software. (Source: Web of Science)



Id	Authors	Values
276	Fraceto, Leonardo F	6
199	de Oliveira, Jhones Luiz	3
247	El-Ramady, Hassan	3
280	Frewer, LJ	3
421	Karunaratne, Veranja	3
455	Kottegoda, Nilwala	3
702	Rai, Mahendra	3
765	Sandaruwan, Chanaka	3
950	Xing, Baoshan	3
975	Zhao, Lijuan	3
1	Abdalla, Neama	2
7	Achete, CA	2
9	Adeleye, Adeyemi S	2
10	Adhikari, Tapan	2
22	Alshaal, Tarek	2
26	Amaratunga, Gehan AJ	2
28	Amer, Megahed	2
40	Archanjo, Braulio S	2
46	Asadishad, Bahareh	2

Figure 3(b) Network of scientific collaboration in the field of nanotechnology and agriculture, 2000-2018 generated by applying Pajek Software (Louvain algorithm community detection)



Id	Countries	Values
17	India	116
51	USA	99
5	Brazil	48
15	Germany	35
18	Iran	34
31	Peoples R China	32
11	Egypt	23
35	Russia	20
21	Italy	14
25	Mexico	14
43	Sri Lanka	14
14	France	13
2	Australia	12
6	Canada	12
12	England	12
32	Poland	12
41	South Korea	12
42	Spain	11
48	Turkey	9
36	Saudi Arabia	7
20	Israel	6
26	Netherlands	6
46	Taiwan	6

Node	Values	Node	Values
	1-39		1-39
	39-78		39-78
	78-116		78-116

Relationship Lines	Values
	1-58
	58-114
	114-171

Figure 3(c) Map of scientific collaboration of agricultural nanotechnology, 2000-2018; with QGIS (QGIS, 2018). Source: Web of Science.

CONCLUSION

Although there is a lack of connectivity in nanotechnology research, the formalization of scientific collaboration networks dedicated to the diffusion of nanotechnology applied to agriculture could demonstrate to governments the importance of promoting investment in research institutes. It is possible to show the increase and direction of research in any field of study.

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11. CONCLUSIÓN

Los materiales con dimensiones nanométricas pueden ser diseñados y sintetizados con propiedades particulares para obtener ventajas competitivas, comparados con materiales similares de dimensiones mayores. Sin embargo, es necesario considerar las implicaciones ambientales, sociales y económicas, e incluso tecnológicas, que podría tener su uso intensivo y extensivo, cuando no existen regulaciones. El efecto tóxico de algunas estructuras nanométricas ha sido ampliamente reportado. Sin embargo, también se han documentado los beneficios potenciales que tienen los materiales de dimensiones nanométricas cuando se aplican a los cultivos en dosis específicas. En este sentido, el efecto de los nanomateriales sobre los cultivos está en función del tipo de material, la dosis aplicada, la vía de administración, el tiempo de contacto nanomaterial-planta, la carga superficial, la etapa fenológica del cultivo, el tipo de cultivo y la presencia, ausencia y tipo de cubierta que tenga el nanomaterial.

En este estudio, la aplicación de 0.15 o 0.30 g de $nTiO_2$ kg^{-1} no afectó el desarrollo de plantas comunes de frijol. La cantidad de $nTiO_2$ aplicada no alteró la estructura de la comunidad bacteriana en el suelo a granel, no rizosférico y rizosférico. El tiempo de exposición tuvo un efecto significativo, en el suelo no rizosférico y rizosférico. El suelo rizosférico se separó claramente del suelo no rizosférico y a granel teniendo en cuenta los filos bacterianos, pero aún más considerando los 50 géneros bacterianos más abundantes.

El uso, eliminación o aplicación de TiO_2 en suelos agrícolas deberá considerar los hallazgos aquí reportados, especialmente en estudios a largo plazo. Además, se deben realizar estudios sistemáticos a largo plazo en terrenos agrícolas para comprender cómo son las interacciones entre las nanopartículas y los microorganismos del suelo, lo cual es importante para una mejor comprensión del peligro o riesgo potencial de estas nanopartículas. Los estudios de nivel de toxicidad deben ser evaluados y mejorados continuamente.

Es importante tener en cuenta que se deben realizar pruebas específicas para cada condición y particularidad con respecto al efecto de los nanomateriales de ingeniería en los cultivos y su impacto en la salud humana y ambiental. Cabe destacar que la evaluación y aplicación de nanomateriales en la agricultura podrían ser de gran valor para reducir la actual escasez mundial de alimentos, pero dichos materiales también podrían comportarse como contaminantes ambientales.

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2. Capítulos de libro

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3. Presentaciones en congresos

Resilience of the rhizosphere bacterial communities from common bean plants *(Phaseolus vulgaris* L.*)* grown in agricultural soil contaminated with TiO_2 nanoparticles. **Gabriela Medina-Pérez**, Yendy E. Navarro-Noya, Fabián Fernández-Luqueño, Claudia L. Ibarra- Sánchez, Jessica N Barrera-Cabrera, Oscar Enrique del Razo-Rodriguez, Luc Dendooven. 12 Congreso Internacional de Biotecnología Vegetal y Agricultura. Del 27 al 31 de mayo, 2019.

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