

NANOCIÊNCIAS E NANOTECNOLOGIA:

Pesquisa e Aplicações

Juan Ramón Collet-Lacoste
(Organizador)



**EDITORIA
ARTEMIS**

2022

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Dados Internacionais de Catalogação na Publicação (CIP)

N186 Nanociências e nanotecnologia: pesquisa e aplicações /
Organizador Juan Ramón Collet-Lacoste. – Curitiba-
PR: Artemis, 2022.

Formato: PDF

Requisitos de sistema: Adobe Acrobat Reader

Modo de acesso: World Wide Web

Inclui bibliografia

ISBN 978-65-87396-66-8

DOI 10.37572/EdArt_290822668

1. Nanociência. 2. Nanotecnologia. 3. Pesquisa. I.
Collet-Lacoste, Juan Ramón (Organizador). II. Título.

CDD 620.5

Elaborado por Bibliotecária Janaina Ramos – CRB-8/9166



PRÓLOGO

Las propiedades particulares de las Nps, muy diferentes en muchos aspectos a las de sus sólidos masivos, han abierto nuevos campos de estudio e investigación a todo nivel: teóricos y aplicados. Son más inestables que los sólidos masivos de los que se diferencian principalmente por su estructura electrónica que no suele ser continua. Esto es una ventaja a nivel de su reactividad y suelen presentar superficies específicas altas que son muy propicias para los procesos de catálisis, un ingrediente muy importante en los procesos cinéticos. Otra propiedad interesante es que no presentan defectos estructurales en su volumen como vacancias o dislocaciones, a diferencia de sus correspondientes sólidos masivos.

Las presentes monografías forman parte del título: “Nanociências e Nanotecnologia: Pesquisa e Aplicações”. Los artículos están ordenados de lo más general (e.g., producción y caracterización de las Nps) a los relacionados con aplicaciones prácticas (e.g., foto catálisis y a su relación principalmente con aplicaciones de origen biológico).

Estos muestran la potencialidad de las nanotecnologías en la comprensión de nuevas aplicaciones en campos tan variados como la catálisis, fotocátalisis, bio-remediación, contaminantes, ambientes acuáticos, antisépticos, bactericidas, virucidas, compuestos bio-activos, biosíntesis extracelular e intracelular, estudio de suelos, vegetales y probióticos, etc.

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USE OF NANOPARTICLES IN THE DEGRADATION OF CONTAMINANTS IN AQUATIC ENVIRONMENTS

Data de submissão: 20/06/2022

Data de aceite: 08/07/2022

Hugo A. Álvarez-Hernández

Laboratorio de Biotecnología Ambiental
Escuela Nacional de
Ciencias Biológicas
Instituto Politécnico Nacional
Ciudad de México, México

Janet Jan-Roblero

Laboratorio de Biotecnología Ambiental
Escuela Nacional de
Ciencias Biológicas
Instituto Politécnico Nacional
Ciudad de México, México
<https://orcid.org/0000-0001-6177-0189>
jjanr@ipn.mx; jjan_r@yahoo.com.mx

Juan A. Cruz-Maya

Unidad Profesional Interdisciplinaria en
Ingeniería y Tecnologías Avanzadas
Instituto Politécnico Nacional
Ciudad de México, México
<https://orcid.org/0000-0001-7635-4954>
jacm.maya@gmail.com

Axel A. Treviño-Trejo

Laboratorio de Biotecnología Ambiental
Escuela Nacional de
Ciencias Biológicas
Instituto Politécnico Nacional
Ciudad de México, México

Oliver Navarrete-Godínez

Laboratorio de Biotecnología Ambiental
Escuela Nacional de
Ciencias Biológicas
Instituto Politécnico Nacional
Ciudad de México, México

ABSTRACT: Food, pharmaceutical, textile industries, among others, are the main sources of environmental contamination due to their untreated wastewater discharge containing toxic compounds to the ecosystem. The increase in the consumption of the products from these industries has caused a serious problem of environmental contamination and it is necessary to take measures to control and eliminate these contaminants. Degradation of contaminants is an alternative to solve this problem, thus, there are conventional methods that are used for this purpose and are categorized into physical, chemical and biological methods. Among the biological methods is bioremediation which consists of using microorganisms or their metabolites for the degradation of contaminants. With the aim of improving bioremediation techniques, currently nanobiotechnology has been proposed as an attractive alternative for its various advantages compared to other techniques. Nanobiotechnology consists of generating nanoparticles of different structures and compositions that are applied to remedy contaminated environments, such as textile dyes in wastewater. The qualities

that hold the nanoparticles are: large surface area, high surface/volume ratio and high adsorption capacity; these qualities provide greater efficiency for the degradation of contaminants in comparison with other methods. This chapter focuses on the different types of nanoparticles that are used in the bioremediation of contaminants in aquatic environmental, such as magnetic nanoparticles, carbon nanoparticles, polymers, titanium or silver nanoparticles. Besides, the use of complex nanoparticles for the immobilization of enzymes that participate in the degradation of contaminants is contemplated. This chapter provides to the reader with an update and a different approach to the contamination problem in aquatic environments.

KEYWORDS: Bioremediation. Contaminants. Aquatic environment. Nanoparticles.

1 CONTAMINATION OF WATER BY XENOBIOTICS

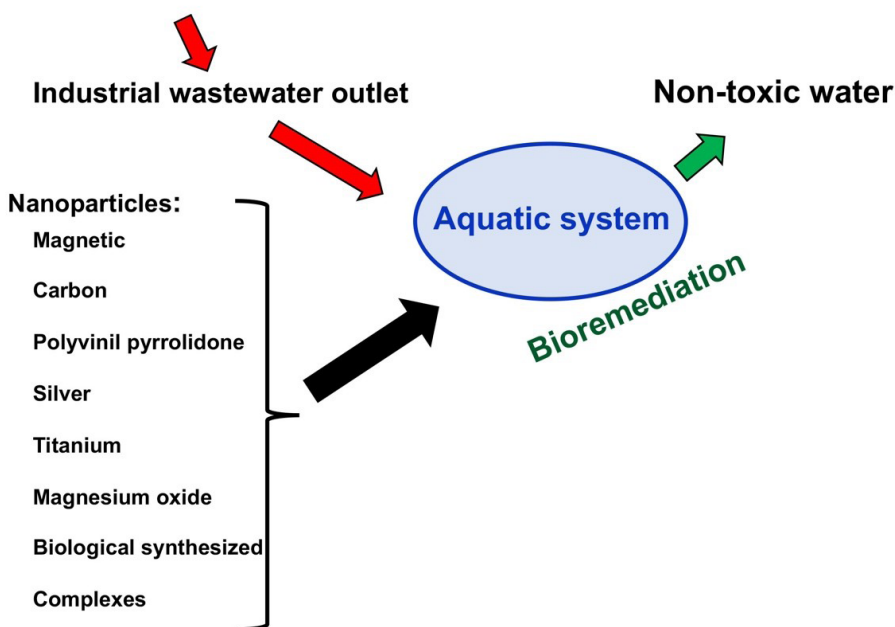
In recent years, textile, pharmaceutical and other industries have contributed enormously to environmental pollution as a result that these industries do not have programs to control the wastewater they generate, this causes untreated wastewater to be released into the environment and cause contamination of water or soil (Karimi-Maleh et al., 2020; Chen et al., 2020). Untreated wastewater discharged into the environment causes the accumulation of pollutants in different environments and these toxic pollutants can reach cities causing an unsustainable problem. To solve the problem of toxic contaminants, it has been proposed to use technologies that degrade or transform contaminants. These technologies are categorized as physical, chemical or biological, and within biological technology is bioremediation. Bioremediation consists of using living organisms or their metabolites that have the capacity to biotransform pollutants into non-polluting (non-toxic) compounds for the environment and that these non-pollutants do not alter the stability of an ecosystem (Garg and Roy, 2022). Microorganisms are living beings with great interest to be used in bioremediation processes, they are ubiquitous and can live anywhere on the planet, which is attributable to their incredible cellular metabolism, which allows them to settle and adapt in a variety of circumstances including environmental pollution. Pollutants can be used by microorganisms as a source of carbon and energy. The isolation of microorganisms with the ability to use or biotransform contaminants is of great interest and they are ideal for the remediation of contaminated environments (Singh and Roy, 2021). Due to this capacity of microorganisms, bioremediation has potential in the destruction, removal, immobilization, or purification of various chemical wastes present in the environment (Karimi-Maleh et al., 2020).

Bioremediation has been applied in contaminated places and used to degrade or biotransform contaminants present in wastewater such as hydrocarbons, oil, heavy metals, pesticides, pharmaceuticals, dyes and other chemicals (Su et al., 2020). Therefore,

the development and implementation of advanced methods for wastewater treatment is a technological priority. One of these scientific advances is the science of nanomaterials or commonly called nanobiotechnology. The construction of materials at the nanometer level has allowed advantages compared to larger-scale materials, since nanomaterials have fundamental changes in their physical and chemical properties and this has generated important advantages for their use in engineering sciences. Nanomaterials have given interesting results such as high efficiency, fast recovery, larger surface areas and nano-adsorbents, and due to these advantages, the use of nanomaterials has been applied in the remediation of contaminants present in water (Anjum et al., 2019). This chapter provides a review of the use of different nanomaterials to effectively bioremediate various xenobiotics in aquatic environments (**Figure 1**).

Figure 1. Schematic illustration of the use of nanoparticles to bioremediate an aquatic environment.

Food, pharmaceutical, textil industry



2 ADVANTAGES OF NANOMATERIALS IN BIOREMEDIATION

The high consumption of dyes, foods, drugs and other industrial compounds has generated a greater production of these, which finally become potential contaminants to the environment, mainly to water. Therefore, there is a growing demand for the use of new technologies for the removal of aquatic contaminants. Nanobiotechnology is a new proposal to solve the problem of water pollution, since it consists of generating

nanoparticles of different chemical composition called nanoparticles, with an ultrafine size, high reactivity and high capacity for interaction with pollutants to detoxify chemical inorganic and/or organic compounds (Brar et al., 2010). An example is iron nanoparticles, which have been widely used in various disciplines as catalysts, sensors, and environmental cleaners due to their ability to adsorb and degrade different water contaminants (Navia-Mendoza et al., 2021); however, they are not the only nanoparticles with these properties, there is currently a wide variety of nanoparticles with their own characteristics that have been used in bioremediation, the different types of nanoparticles will be mentioned below.

3 MAGNETIC NANOPARTICLES

Iron oxide nanoparticles (Fe_3O_4) have magnetic properties and are used as magnetic sources for the removal of textile dyes (Hojjati-Najafabadi et al., 2022). The principle of contaminant removal consists of a magnetic separation by the iron oxide nanoparticle where the contaminant is extracted from the aquatic environment; the use of iron oxide nanoparticles is low cost, biocompatible, highly stable and easy to synthesize (Zhang et al., 2021). A disadvantage of the use of this nanoparticle is its high surface energy and magnetic attractive force, due to this, magnetic nanoparticles tend to lose their magnetic property and will agglomerate in aqueous solution, however, a resolving alternative is to cover the surface of the magnetic nanoparticle with layers of active compounds to improve its properties.

4 CARBON NANOPARTICLES

These nanoparticles are made of carbon nanofibers and carbon nanotubes that have carbon molecules firmly held together by covalent bonds. Carbon nanoparticles have the ability to adsorb molecules due to their hydrophobic properties, by covalent bonds, or by electrostatic effects (Saifuddin et al., 2013). Carbon nanoparticles have high capacities for the adsorption of compounds and also have a high affinity for polluting compounds such as textile dyes. The disadvantage of the use of carbon nanoparticles is that they are relatively expensive, which limits their use for the adsorption of pollutants from wastewater (Cai et al., 2017).

5 NICKEL POLYVINIL PYRROLIDONE NANOPARTICLES

Chemical derivatives of nickel polyvinyl pyrrolidone have been used to produce nanoparticles and these nanoparticles have the ability to remove textile dyes from

aqueous solutions with a removal efficiency of 98.7% in 120 min (Kale and Kane, 2017). The size and shape of the nanoparticles made with polyvinyl nickel pyrrolidone observed under transmission electron microscopy show a dispersion in the nanoparticle matrix and with a size of 20-44 nm.

6 SILVER NANOPARTICLES

Silver nanoparticles have a strong antibacterial effect and have been used for this purpose in microbiology. They have catalytic capacity towards textile dyes although their degradation capacity is low, consequently their use is not convenient. In addition, silver nanoparticles mounted on silicone disks prevent bacterial contamination in the environment, which is another particularity of these nanoparticles (Marimuthu et al., 2020).

7 TITANIUM NANOTUBES

Titanium or titanium dioxide (TiO_2) is of considerable interest since these compounds have the ability to generate photocatalysis; due to the low price of these compounds, they are good candidates for the degradation of pollutants. Photocatalysis is a process that occurs during the degradation of xenobiotics such as textile dyes. In addition, because the nanoparticles have large surface areas, they achieve high photocatalysis efficiencies and therefore high percentages of dye degradation. The generation of titanium nanoparticles with large and specific surface area is by means of the Kasuga's technique, this technique produces titanium nanotubes with a homogeneous structure. Kasuga's technique consists of using sodium-titanium hydrides, producing sodium particles that are localized on top of the nanotube, as well as in the gaps in the nanotube walls. In addition, an aqueous solution of HCl or other cations removes the sodium particles from the walls of the nanotube. The presence of residual sodium inside the TiO_2 nanotube is relevant since it confers adsorption capacities very equivalent to the activity of carbon, thus being the property of removal of contaminants by these titanium nanotubes in addition to the photocatalytic activity (Sandoval et al., 2017).

8 NANOPARTICLES OF MAGNESIUM OXIDE (MgO)

MgO nanoparticles have adsorption properties of xenobiotic compounds, for example Reactive Black 5 and Reactive Orange 122 dyes are efficiently adsorbed at 500 and 333.34 mg/g, respectively, by MgO nanoparticles (Randiligama et al. 2020).

9 BIOLOGICALLY SYNTHESIZED NANOPARTICLES

Nanoparticles can be synthesized using biological agents as the main support and these nanomaterials can also include metal compounds as well as metal oxides. Nanoparticles generated by biological agents can be used in the degradation of xenobiotics such as textile dyes. Plants, bacteria and fungi are the potential raw material for the synthesis of nanomaterials of biological origin, since these living beings produce bioactive compounds. The bioactive compounds produced by these biological entities facilitate the formation of nanomaterials because these bioactive compounds play a key role in nanoparticle stability and reduction. For example, *Cassythia filiformis* is used to synthesize silver nanoparticles, *Cynara cardunculus* for the synthesis of Fe_3O_4 nanoparticles, or *Pseudomonas putida* for Bio-nanoPb (Bhakya et al., 2015).

10 NANOPARTICLE COMPLEXES WITH ENZYMES/MICROORGANISMS

Another application of nanoparticles is to use them as supports to immobilize compounds, enzymes or microorganisms; enzymatic immobilization by nanoparticles increases the reaction efficiency compared to that compounds, enzymes or microorganism in free form (not immobilized). In particular, nanoparticles have been used as a support to immobilize enzymes, especially enzymes that participate in the degradation of xenobiotics. The immobilization of enzymes by nanoparticles can be achieved by different methods, such as covalent binding of the enzyme to the nanoparticle, physical adsorption, encapsulation of the enzyme by the nanoparticle, entrapment of the enzyme, and cross-linking with the target enzyme. Of all the methods, physical adsorption is the simplest and most common (Bilal et al., 2018). The choice of the structure and composition of the nanoparticle is important for successful enzymatic immobilization, since some nanoparticles with unsuitable structures or compositions can inhibit or denature the enzyme that is immobilized in the nanoparticle. The nanoparticles of choice to immobilize enzymes are those nanoparticles made of sodium alginate, agarose, chitin/chitosan, polyvinyl alcohol, polyacrylamide, macropores of ion exchange resins, hydrophobic gel-solutions, carbon nanotubes and nanopores of silica gel (Bilal et al., 2019).

In addition, the bifunctional nanoparticles have a double function, support and an additional function; such as the photocatalysis-type nanoparticles that have an immobilized enzyme that participates in the degradation of the contaminant. In this way, the degradation of the contaminant is carried out by the photocatalysis of the nanoparticle itself and by the enzymatic activity given by the immobilized enzyme. Some photocatalytic nanoparticles are made with graphitic carbon nitride modified titanium oxide (TiO_2/g -

C₃N₄), or molybdenum oxide modified with copper sulfide and sulfide (MoO₃@MoS₂-CuS), or titanium oxide (TiO₂), or silver-modified titanium oxide and zinc oxide (ZnO), among others. These are widely used as a support to immobilize enzymes and are very abundant in nature, they are low cost, non-toxic and have a high oxidation power (Acharya et al., 2018). However, these nanoparticle matrices have limitations since they can denature the immobilized enzyme, or the enzyme is affected by exposure to the solvent, or the lack of reuse of the nanoparticle.

As mentioned, enzymatic immobilization by nanoparticles is of great interest for nanobiotechnology in the treatment of contaminated wastewater, for this reason immobilizing the enzymes that participate in the degradation of textile dyes has been one of the main approaches. The removal of inorganic and organic dyes in wastewater has been achieved by the immobilization of the peroxidase enzyme on carbon-based nanoparticles; carbon nanoparticles can be carbon nanotubes, carbon nanosheets, and carbon nanoparticles, or metal-based nanoparticles, polymer-based magnetic nanoparticles, and zero-valence nanoparticles (Mehmood et al., 2021). Example of metal-based nanoparticles include iron oxide nanoparticles and their modified forms, such as maghemite nanoparticles, starch functionalized maghemite nanoparticles, magnetite nanoparticles, magnetite nanospheres and ethylenediamine functionalized nanochains, among others, which are used as supports for the immobilization of peroxidase.

Other enzymes that have been immobilized with nanoparticles are lipases and laccases, these enzymes participate in the degradation of microplastics. The nanoparticles used as a support for the immobilization of the enzyme are inorganic and organic. Inorganic nanoparticles have gained recognition for immobilizing lipases or laccases due to their thermal, mechanical, and chemical stability compared to organic nanoparticles (Hartmann and Kostrov, 2013). In addition, inorganic nanoparticles have the advantages of having a well-defined porous geometry and good distribution, large surface area, and a high surface/volume ratio, which contributes to a higher loading capacity of the immobilized enzyme (Zhou et al., 2013).

With respect to organic nanoparticles, carbon-based nanoparticles are preferred for immobilizing lipases and laccases. While inorganic nanoparticles have gained popularity in recent years. However, carbon-based nanoparticles are of great interest, particularly carbon nanotubes, whose use is common to immobilize enzymes such as lipases and laccases, and this is because they have a modifiable surface, a high surface/volume ratio, as well as, they have chemical, thermal and mechanical stability (Cacicedo et al., 2019). There are two types of carbon nanotubes, single-walled and multi-walled.

The first consists of a single layer of graphite with a central tube; while the second, the multiwall, has multiple layers of graphite around the central tube (Feng and Ji, 2011).

Other carbon-based materials that are also used to immobilize enzymes are those made from chitosan, polymer-crosslinked macropores, and resins (Su et al., 2018). However, the immobilization of enzymes by carbon-based nanoparticles significantly enhances contaminant-degrading activities. The efficiency of this activity frequently relies on meticulous care during the synthesis of the immobilized nanoparticle-enzyme complex, since a good enzymatic immobilization ensures the success of the activity under experimental and environmental conditions. In addition, it is desirable that the immobilization of the enzyme can be reused several times so that its application is achievable in the bioremediation of contaminated water.

11 CONCLUSION

Nanomaterials offer an alternative for the remediation of polluted water; however, further studies are required to have better efficiency in the degradation of pollutants in the environment. In addition, it is required to synthesize modified nanoparticles with greater effectiveness, high efficiency, friendly to the environment, easy to handle and low cost. More studies in nanobiotechnology are necessary to apply these technologies in ecosystems and their commercialization in the remediation of contaminated sites, however, the different existing nanoparticles generate a range of possibilities to solve particular problems of water pollution.

12 ACKNOWLEDGMENTS

This work was supported by Instituto Politécnico Nacional (IPN), Secretaría de Investigación y Posgrado (SIP) grant 20220781. The work was carried out during the sabbatical year granted by the IPN to JJR, who is grateful for this support provided. JJR and JACM are grateful for the support provided by IPN through the EDI and COFAA sponsorships and for the SNI-CONACYT award.

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SOBRE EL ORGANIZADOR

El Dr. Juan Ramón Collet-Lacoste es licenciado en ciencias químicas de la Universidad de Buenos Aires (UBA) y PhD de la Universidad de Paris Sud (XI). Su especialidad es la físico química, en la rama de la termodinámica de los procesos irreversibles (TPI), especialmente en el estudio de los procesos cinéticos en los sistemas electroquímicos.

Ha desarrollado varios trabajos relacionados a los mecanismos de reacción y transporte de materia sobre electrodos metálicos, así como el desarrollo de electrodos para celdas de combustible de baja temperatura (fuel cells).

Es un especialista en la técnica de impedancia electroquímica, en la cual ha publicado varios artículos en revistas internacionales.

Desde el punto de vista experimental, ha trabajado en el desarrollo de celdas de combustible con Nps de platino y paladio y de electrolizadores alcalinos de baja temperatura.

Actualmente realiza trabajos sobre la oxidación acuosa del aluminio en gradientes de temperatura. Este trabajo esta relacionado a los elementos combustibles de los reactores experimentales multipropósito para la fabricación de radioisótopos de uso médico.

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