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Essay

Immobilized nanomaterials for arsenic removal in agricultural systems: a brief review

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Abstract

Arsenic contamination in agricultural soils and irrigation water poses a significant threat to crop productivity and food security. In response to this problem, the present review aimed to analyze the use of immobilized nanomaterials as a technological alternative for the efficient removal of arsenic contamination in agricultural systems. Recent studies on the application of nanomaterials, such as zero-valent iron nanoparticles, nanoclays, and metal oxides, immobilized in polymeric, ceramic, or natural matrices, were collected and evaluated. The methodology consisted of a documentary and comparative analysis of scientific research published in peer-reviewed journals, considering the parameters of adsorption capacity, removal mechanisms, optimal conditions, and efficiency in the field. The results indicated that the immobilized nanomaterials have greater stability, regenerative capacity, and lower leaching risk compared to traditional methods. In addition, successful cases were documented in Mexico, where their implementation reduced the concentration of arsenic contamination in soils and irrigation water by up to 70%. It is concluded that the use of immobilized nanomaterials is a viable and sustainable strategy for agricultural decontamination; nevertheless, more studies on their environmental impact and cost-benefit are still required for their large-scale application.

Keywords:

immobilized nanomaterials, remediation of As, sustainable agriculture.

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The presence of arsenic (As) in soils and irrigation water poses a critical threat to sustainable agriculture, crop quality, and public health. Regions such as Mexico, India, Bangladesh and Chile have reported high concentrations of As within the food security supply (Bhattacharya *et al*., 2010; Ruiz-Huerta *et al*., 2017). In addition, As is highly toxic and mobile in agricultural environments. For this reason, organizations such as the World Health Organization (WHO) and the Food and Agriculture Organization of the United Nations (FAO) have established permissible limits on water, soil, and food to reduce the associated risks.

In Mexico, the NOM-127-SSA-2021 and NOM-147-SEMARNAT/SSA1-2004 standards regulate the presence of As in drinking water and agricultural soils, establishing maximum values between 0.025 mg L^{-1} in water and 22 mg kg^{-1} in soils (Secretaría de Salud, 2022; SEMARNAT, 2007). Although there are traditional removal methods, such as coagulation, filtration, and ion exchange, they present limitations in efficiency and costs (Kumar *et al*., 2019).

Faced with this scenario, nanotechnology has emerged as a promising alternative, especially through the use of immobilized nanomaterials, which offer greater selectivity, stability, and efficiency in the adsorption of As. Therefore, this article presents a critical review of the use of immobilized nanomaterials in the remediation of soil and irrigation water contaminated with As, including case studies, mechanisms of action, technological comparisons, and their environmental assessment.

Development

Impact of arsenic on agriculture

Arsenic in agricultural soils compromises ecosystem health and crop productivity (Ruíz-Huerta *et al*., 2017). In Mexican regions such as La Comarca Lagunera, the use of water contaminated with As has been shown to modify the pH, reduce the availability of essential nutrients, and affect the soil microbiota, decreasing the quality of the crops and increasing their toxicity by bioaccumulation (Osuna-Martínez *et al*., 2021).

Sources of arsenic in agricultural systems

As has both natural and anthropogenic origins. In its natural form, it is released by the erosion of arsenical minerals (arsenopyrite), volcanic activity, and the dissolution of minerals in aquifers rich in As. On the other hand, anthropogenic sources include the use of arsenical pesticides, contaminated fertilizers, irrigation with contaminated groundwater, mining activity, and industrial waste (Jiménez *et al*., 2023). Figure 1 summarizes these sources.

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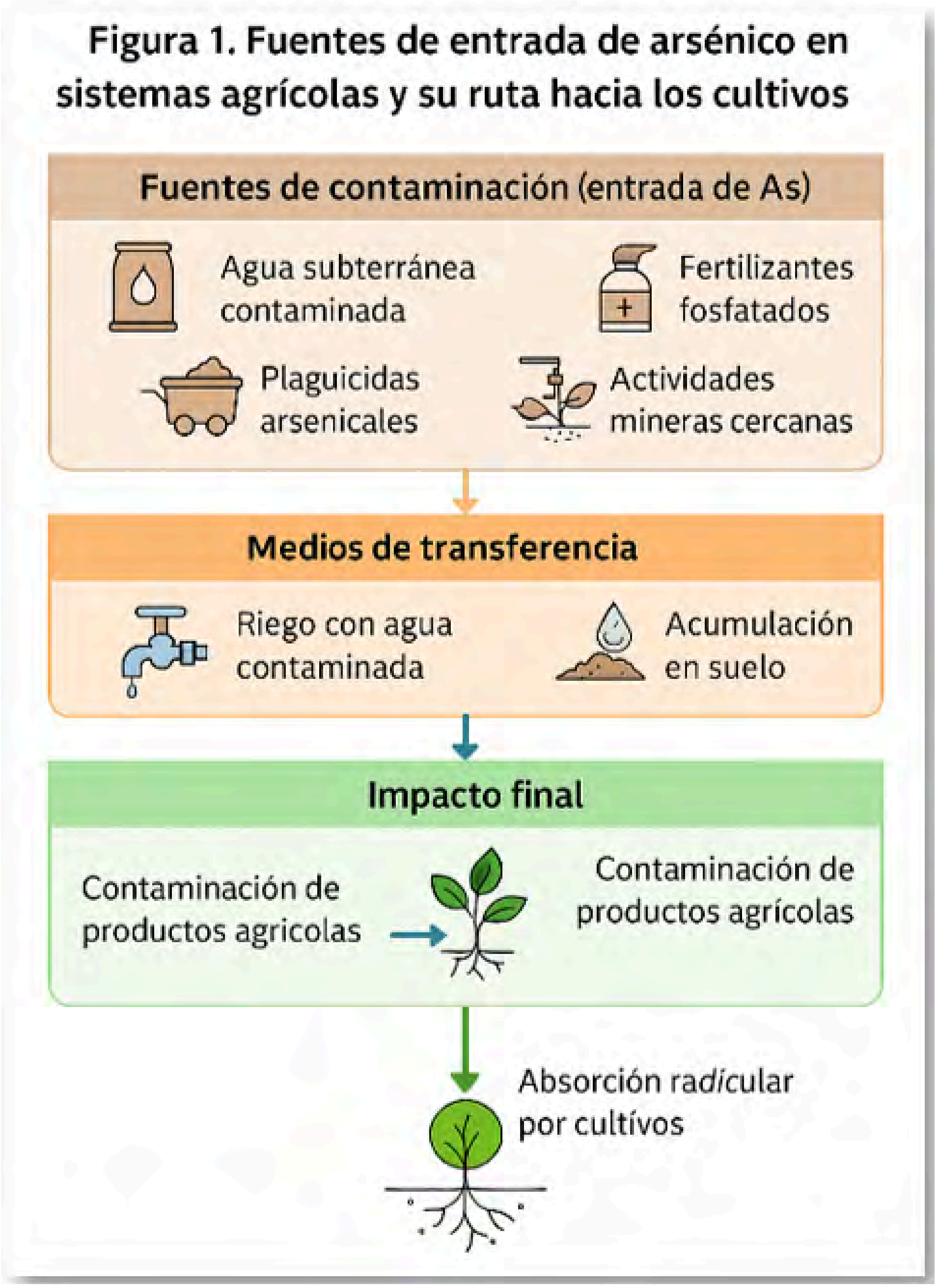
Figure 1. Sources of As in agricultural systems.



Effects of As on soil fertility

As directly interferes with agricultural soil dynamics, namely: microbiota, it inhibits beneficial bacteria and fungi, such as *Rhizobium* and *Mycorrhizae*, affecting nitrogen and phosphorus cycles, and reduces microbial biodiversity. Soil pH: in acidic soils, As has greater mobility and bioavailability; in alkaline soils, it can form complexes that immobilize nutrients. Essential nutrients: it competes with phosphorus and decreases the availability of iron (Fe), zinc (Zn) and manganese (Mn), altering metabolic processes, such as photosynthesis and protein synthesis (Singh and Srivastava, 2020; Beniwal *et al*., 2023).

Revista Mexicana de Ciencias Agrícolas REMEXCA
DOI: https://doi.org/10.29312/remexca.v16i30.4056

Crop contamination and food security

As bioaccumulates in edible crops, affecting their nutritional value and generating toxicological risks in living beings. Its absorption depends on the physiological characteristics of the crop. Table 1 details the most affected crops and their associated risks, including rice, wheat, maize and vegetables.

Table 1. Crops most affected by the absorption of As.

Crop	Description	Damage or specific impacts of As on the crop	Effects on health	Reference
Rice (*Oryza sativa* L.)	Crop highly susceptible to As due to its growth in flooded soils, where As^{+3} is more soluble and bioavailable.	Alteration in silicon metabolism, oxidative stress, inhibition of root growth, and lower grain yield.	Prolonged exposure can cause skin, lung, and bladder cancer, in addition to affecting the nervous and cardiovascular systems.	Mitra *et al*. (2017);FAO (2022)
Wheat (*Triticum* spp.)	It absorbs As to a lesser extent than rice, but it can accumulate it in grains and reduce nutritional quality.	Reduction in germination, lower aerial and root biomass, and interference in phosphorus metabolism.	It can affect the bioavailability of iron and zinc, increasing the risk of anemia and nutritional deficiencies.	Bhattacharya *et al*. (2010)
Corn (*Zea mays* L.)	A basic food crop in Mexico; it absorbs As from the soil and irrigation water, with accumulation in roots, leaves, and grains.	Damage to vascular tissues, reduction of chlorophyll, reduced leaf growth, and accumulation of As in grains.	Prolonged consumption can generate metabolic alterations, lower development in children, and liver and kidney problems.	Huerta and Hernández (2012)
Root vegetables (carrot, potato, beet)	They grow in direct contact with contaminated soils, which facilitates the absorption of As in their tissues.	Effects on the quality of the tuber, morphological deformations, and accumulation of As in edible tissues.	It causes chronic toxicity, affecting the digestive system and the absorption of essential nutrients.	Upadhyay *et al*. (2019)
Leafy vegetables (spinach, lettuce, chard)	They absorb As through irrigation water, accumulating it in leaves and reducing its nutritional quality.	Chlorosis, marginal necrosis, including water stress and decreased protein and antioxidant content.	The accumulation in leaves can cause mild to moderate poisoning, affecting the nervous and hepatic systems.	Laizu (2008)

Impact on the nutritional quality of food

Beyond its toxicity, As deteriorates the nutritional quality of food by altering plant metabolism.

Nutrient absorption

It competes with phosphorus and reduces the availability of Fe, Zn and Mn, affecting growth and nutritional content (Beniwal *et al*., 2023).

DOI: https://doi.org/10.29312/remexca.v16i30.4056

Chemical composition

It affects the synthesis of proteins, sugars, and antioxidants, which deteriorates the energy value, flavor, and quality of the food (Huerta and Hernández, 2012; Ruíz-Huerta *et al*., 2017; Upadhyay *et al*., 2019; Beniwal *et al*., 2023).

Availability in humans

It reduces intestinal absorption of minerals, increasing the risk of anemia, immunodeficiencies and bone diseases (Camacho *et al*., 2011; Singh and Srivastava, 2020).

Documented cases and crops affected in the world

Studies in Bangladesh, India, Argentina, Mexico and other countries show that the As present in soils and irrigation water has caused severe effects on crops and public health. Table 2 summarizes these cases, showing their geographical distribution, crops involved, and health consequences, such as hydroarsenicism, cancers and nutritional deficiencies (Bhattacharya *et al*., 2010; Alarcón Herrera *et al*., 2020).

Table 2. Impact of As on agricultural crops.

Country	Situation	Crops affected	Impacts on health	Reference
Bangladesh/India	Groundwater contamination with As (drinking water and crops)	Rice	Skin, lung, and bladder cancer (CA), cardiovascular (CV) disease, and diabetes.	Bhattacharya *et al*. (2010); Mitra *et al*. (2017)
Argentina/Mexico	High concentration of As in irrigation water	Corn and vegetables	Chronic hydroarsenicism (CH), bladder, kidney, and lung CA; 4 million people exposed.	Laizu (2008); Huerta and Hernández (2012)
Chile	As contamination (mining) in water and soil	Vegetables and fruits	Regional increase in rates of CA and CV diseases.	Upadhyay *et al*. (2019)
Mexico	High levels of As in water in agricultural areas	Corn and beans	HC, high risk of CA: rural communities affected.	Huerta and Hernández (2012); Alarcón-Herrera *et al*. (2020)
United States of America	Presence of As in wells, in agricultural regions.	Rice	Risk of CA and CV diseases from consumption of contaminated rice: thousands exposed.	Meharg *et al*. (2009); USGS (2018)

As in agricultural systems not only compromises crop yields, but also decreases their nutritional value, puts public health at risk, and limits food security in rural areas.

Removal of As in irrigation water using immobilized nanomaterials

The use of immobilized nanomaterials has emerged as an innovative strategy in agricultural remediation, offering efficient and sustainable solutions to remove As in soils and irrigation water. Their integration into solid matrices improves stability, facilitates recovery, and allows controlled application in the field.

Zero-valent iron nanoparticles

Nanoparticles (NPs) of zero-valent iron (nZVI) have been used for the decontamination of water from both heavy metals and chlorinated organic compounds, due to their high reactivity

DOI: https://doi.org/10.29312/remexca.v16i30.4056

and adsorption capacity. The immobilization of these NPs in solid matrices, such as polymers or inorganic supports, improves their stability and facilitates their application in agricultural environments.

Findings such as those by Qu *et al*. (2019) showed that nZVI immobilized in a chitosan matrix were effective in reducing hexavalent chromium (Cr(VI)) in contaminated soils, achieving a significant decrease in Cr(VI) concentration in a short period (Qu *et al*., 2019). At the same time, in China, the application of immobilized nZVIs in agricultural soils contaminated with As resulted in a 70% reduction in the concentration of As available, improving soil quality and crop safety.

Nanoclays

Nanoclays, such as montmorillonite, bentonite, and other smectic clays, have been used for soil remediation due to their high specific surface area and cation exchange capacity, properties suitable for adsorbing pollutants and improving the physical properties of the soil. Their immobilization in organic or inorganic matrices allows for more controlled and efficient application (Almasri *et al*., 2018; Baigorria *et al*., 2021).

In this sense, the incorporation of nanoclays in soils contaminated with organochlorine pesticides showed an 85% reduction in the concentration of these compounds, in addition to improving water retention and soil structure. In addition, in Spain, the application of immobilized nanoclays in grape-growing soils contaminated with copper led to a 60% decrease in the concentration of available copper, promoting the recovery of the soil microbiota and the health of the vines.

Metal oxides

Nanocomposites of metal oxides, such as zinc oxide (ZnO) and magnesium oxide (MgO), possess antimicrobial and contaminant-adsorption properties. Their immobilization in polymeric or ceramic matrices makes it possible to use them in the remediation of soils and agricultural water (Gao *et al*., 2021). The application of ZnO nanocomposites immobilized in an alginate matrix showed efficacy in the removal of pathogenic bacteria and the adsorption of heavy metals in irrigation water (Gao *et al*., 2021).

In Mexico, the use of ceramic filters impregnated with metal oxide nanocomposites allowed the purification of irrigation water with water quality problems. In regions such as Coahuila and Durango, the implementation of irrigation water remediation technologies has shown positive results. The use of iron oxides, such as Fe_3O_4 or Fe_2O_3, immobilized in filtration systems has significantly reduced the levels of As in water for the irrigation of corn and wheat crops (Morales *et al*., 2012).

For example, in Guanajuato, Mexico, the use of natural zeolites has helped improve the quality of irrigation water in areas affected by contamination with different heavy metals; this method has allowed farmers to reduce the levels of heavy metals in crops, thus ensuring greater food security (Armienta *et al*., 2020).

Immobilized TiO_2 NPs are known for their photocatalytic properties, used for the degradation of organic pollutants in water and soil (Yu *et al*., 2013). The immobilization of TiO_2 NPs in solid supports prevents their dispersion in the environment and facilitates their recovery. One study reported that TiO_2 immobilized in silica spheres was effective in the degradation of pesticides in irrigation water, achieving a removal of 90% of contaminants under solar irradiation (Yu *et al*., 2013).

Adsorption mechanisms and efficiency of nanomaterials

The removal of As in soils and irrigation water by nanomaterials occurs through various physicochemical mechanisms that depend on the composition, structure, and functionalization of the materials. The interaction between As and nanomaterials determines their adsorption efficiency, influenced by pH, As concentration, competition with other ions, and the stability of the nanomaterial in the agricultural environment. The main mechanisms of adsorption of As by nanomaterials include the following.

Revista Mexicana de Ciencias Agrícolas
DOI: https://doi.org/10.29312/remexca.v16i30.4056

Ion exchange

It involves the substitution of arsenical ions on the surface of the nanomaterial (eg., functionalized iron oxides), common in modified zeolites and nanoclays.

Chemisorption

It is the formation of strong stable or coordinated covalent bonds, especially in nZVI (Fe^0) and some metal oxides, such as Fe_3O_4 and MnO_2. nZVI acts mainly by reducing As^{+3} to insoluble forms and chemisorption on iron oxides formed *in situ*.

Electrostatic adsorption

It attracts arsenical species with opposite charge, depends on pH, and is common in nanocomposites functionalized with amino groups, such as nanoclays with organic modifications and nanoparticles doped with biopolymers. In the case of nanoclays such as montmorillonite, it retains As^{+5} by ion exchange with anions such as phosphate or sulfate.

Photocatalysis

In the case of immobilized TiO_2 NPs, they oxidize As^{+3} to As^{+5} and promote its subsequent adsorption on the active surface, degrading associated organic compounds, which facilitates the adsorption of As by light-assisted oxidation.

Physical entrapment

In porous matrices, such as ceramic or polymeric supports, that increase As retention by diffusion and retention in internal channels.

Figure 2 is a schematic representation of the main physicochemical adsorption mechanisms involved in the removal of As by immobilized nanomaterials: chemisorption in TiO_2 NPs, electrostatic adsorption in nanoclays, ion exchange in clays, and oxidation processes in the presence of Fe NPs. The structures reflect interactions at the molecular level typical of each system.

Revista Mexicana de Ciencias Agrícolas
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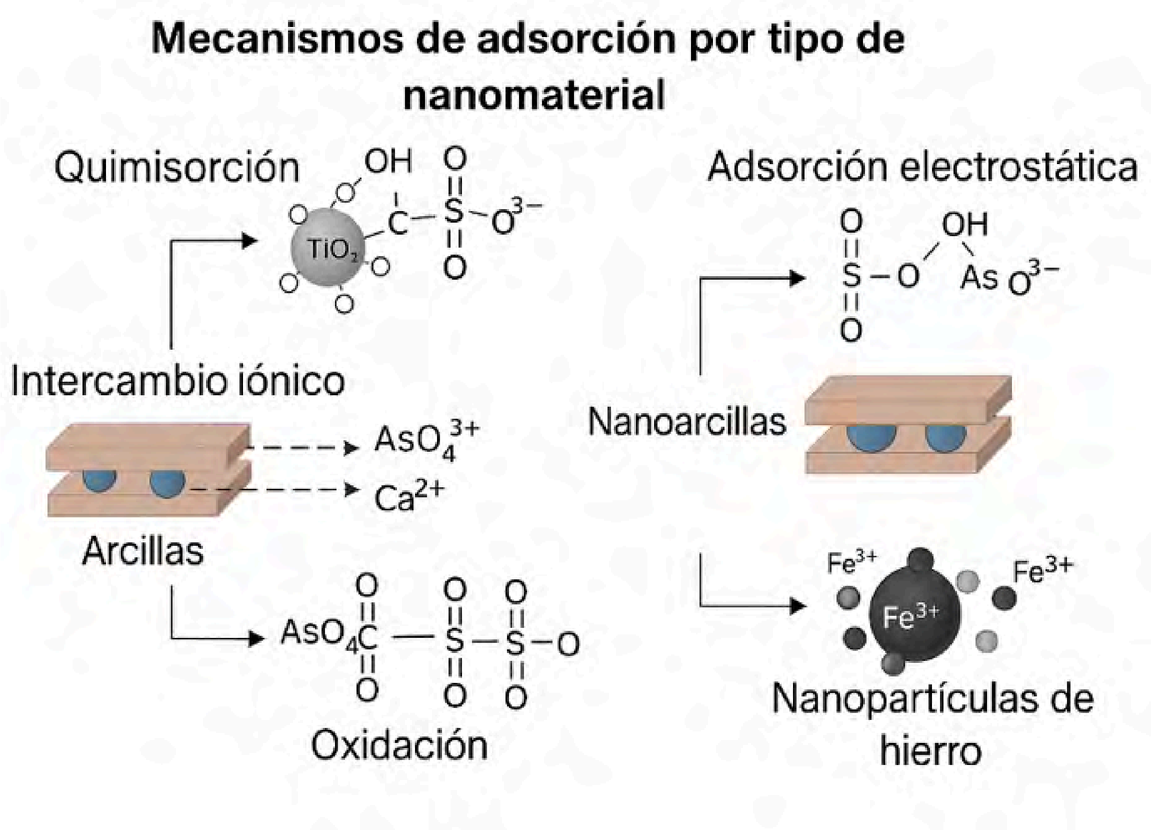
Figure 2. Arsenic adsorption mechanisms according to the type of nanomaterial immobilized.



These mechanisms together allow the immobilized nanomaterials to overcome the technical limitations of traditional methods; the efficiency depends on the type of nanomaterial, the arsenical species (As^{+3} or As^{+5}), pH, ionic competence, or environmental conditions. Unlike methods such as coagulation, ion exchange, or phytoremediation, immobilized nanomaterials have greater efficiency (approximately 95%), less waste generation, and a potential for reuse and regeneration. Table 3)presents some materials that overcome the technical and environmental limitations of traditional technologies.

Table 3. Adsorption capacity of As in immobilized nanomaterials.

Nanomaterial	Adsorption capacity (mg As g^{-1})	Adsorption mechanism	Optimal conditions (pH, temperature, etc.)	Reference
Zero-valent iron NPs (nZVI)	40-70	Chemisorption and ion exchange	pH 6-8, aerobic conditions	Kang *et al*. (2019);Qu *et al*. (2019)
Doped manganese oxides	30-60	As^{+3} oxidation and electrostatic adsorption	pH 4-7, moderate temperature	Xie *et al*. (2022)
Carbon nanocomposites	25-55	Electrostatic adsorption and chemisorption	pH 6-9, presence of organic matter	Toor *et al*. (2015); Gautam *et al*. (2021)
Immobilized TiO_2 NPs	15-40	Photocatalysis and surface adsorption	pH 5-7, moderate solar irradiance	Yu *et al*. (2013).
Nanoclays (montmorillonite)	10-35	Cation exchange and adsorption by a charged surface	pH 4-6, moderate humidity	Almasri *et al*. (2018); Baigorria *et al*. (2021)

DOI: https://doi.org/10.29312/remexca.v16i30.4056

Nanomaterial	Adsorption capacity (mg As g^{-1})	Adsorption mechanism	Optimal conditions (pH, temperature, etc.)	Reference
Modified natural zeolites	20-50	Ion exchange and entrapment in crystal channels	pH 6-8, field conditions	Morales *et al*. (2012); Armienta *et al*. (2020)

Case studies in Mexico

Various nanomaterials have been used effectively to remove heavy metals from water and soils in several regions of the country. In Durango, NPs of oxides and activated carbon filters have been used, with efficient results in the adsorption of As and Pb, reducing their solubility (García and Bonilla, 2015; Zhao *et al*., 2020). In Guanajuato, natural zeolite filters have been shown to have a high capacity to trap As and Hg in their pores (Sridhar and Adeyemo, 2009; Morales *et al*., 2012).

Likewise, in Coahuila, biofilters combined with iron NPs have been developed to remove As and Cd through biological processes assisted by microorganisms (Finnegan and Chen, 2012; Wang *et al*., 2022). In Hidalgo, the use of activated carbon with NPs has shown high efficiency in removing Pb and Hg, improving the adsorbent properties of the system (Lui *et al*., 2021; García and Pérez, 2021).

At the same time, in San Luis Potosí, good results have been reported in phytoremediation systems with carbon nanofilters, which allow the retention of As and Pb in combination with plants that absorb pollutants (López and Martínez, 2020; Zhao *et al*., 2020). In Sonora, nanoclays functionalized with amino groups have shown great capacity to reduce the availability of As and Pb in agricultural soils (Martínez *et al*., 2020).

Finally, in Querétaro, manganese oxides doped with iron NPs have been effective in stabilizing As and Cd in contaminated soils (Figure 3) (Ramírez *et al*., 2021). These applications have not only demonstrated technical efficiency, but have also contributed to improving environmental health and quality of life in rural communities exposed to high levels of As. In several cases, there has been a reduction in diseases associated with the consumption of contaminated water and an increase in farmers' confidence in the safe use of water resources for their crops.

Revista Mexicana de Ciencias Agrícolas
REMEXCA
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Figure 3. Geographic distribution of documented applications of immobilized nanomaterials for As removal in Mexico.

Comparison with traditional methods in arsenic removal

Historically, As in agricultural systems have been treated with conventional methods, such as chemical coagulation, activated carbon filtration, ion exchange, and phytoremediation. However, these approaches have significant limitations: low efficiency at low concentrations and difficulty in scaling in the field.

In contrast, immobilized nanomaterials offer key advantages: higher adsorption efficiency (up to 95%), low environmental impact, and possibly regeneration. Immobilized in supports such as biopolymers, zeolites, or biochar, they improve stability, reduce leaching, and facilitate recovery. Table 4 shows a comparison between traditional methods and immobilized nanomaterials considering efficiency, cost, and sustainability.

Table 4.
Comparison of traditional methods vs immobilized nanomaterials.

Method	Efficiency (%)	Cost in dollars ($ m^{-3} treated)	Limitations	Environmental impact	Reference
Coagulation with iron salts	50-70	1.5-3	It generates toxic sludge	Moderate (waste management)	WHO (2022); Smith *et al*. (2019)
Activated carbon filtration	30-50	0.5-1.2	Less effective in water with organic matter	Low	Meharg *et al*. 2017); Zhao *et al*. (2018);FAO (2022)
Ion exchange	60-80	2-4	It requires resin regeneration	Chemical waste generation	Kim and Benjamin (2004)
Phytoremediation	20-40	0.3-1	Slow process	Beneficial (biomass absorption)	Atabaki *et al*. (2020); Alka *et al*. (2021)

DOI: https://doi.org/10.29312/remexca.v16i30.4056

Method	Efficiency (%)	Cost in dollars ($ m^{-3} treated)	Limitations	Environmental impact	Reference
Immobilized nanomaterials	70-95	2.5-4.5	It requires optimization in the field	Low (it can be regenerated and reused).	Yu *et al*. (2013); Qu *et al*. (2019); Rao Vaddi *et al*. (2024)

Environmental assessment of immobilized nanomaterials

Despite their efficiency, the use of nanomaterials requires a comprehensive assessment to ensure their compatibility with the agricultural environment and consider the following sub-themes.

Biodegradability

Nanomaterials based on biopolymers such as chitosan or cellulose are preferable, as they degrade naturally without leaving any lingering residues. Instead, metal nanoparticles can accumulate and alter soil structure in the long term.

Toxicity to the microbiota

Some nanoparticles (e.g., silver, Zn, or Ti oxides) have antimicrobial properties that can reduce beneficial soil populations, such as nitrogen-fixing bacteria or mycorrhizae. It is recommended to use natural supports to minimize their toxicity.

Leaching risk

Unstabilized nanomaterials can migrate into nearby bodies of water. Their immobilization in solid matrices reduces this risk, keeping the material at the application site and preventing secondary contamination.

Ecological risks

Although immobilized nanomaterials present techniques, they also involve ecological risks that must be considered before their large-scale application. One of the main ones is the alteration of the soil microbiota, since some nanomaterials, such as zinc and silver oxides, have antimicrobial properties that can reduce populations of beneficial microorganisms, such as nitrogen-fixing bacteria or mycorrhizae.

In addition, if not properly stabilized, nanomaterials can migrate into the environment, accumulate in sensitive areas, such as bodies of water or non-target plant roots, and modify essential soil processes. This mobility and environmental persistence could generate indirect ecotoxic effects on the food chain.

Mitigation strategies

To minimize these risks, it is recommended to prioritize the use of biocompatible or biodegradable matrices, such as chitosan, cellulose, or alginate, which reduce toxicity and improve the retention of the nanomaterial at the application site. Likewise, post-application environmental monitoring protocols should be established, which include bioassays on soil microorganisms, leachate analysis, and evaluation of changes in soil physicochemical properties.

Finally, the use of nanomaterials in agricultural systems must be regulated by regulatory frameworks that ensure a safe, sustainable, and socially acceptable application, especially in regions with high environmental vulnerability.

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Conclusions

Immobilized nanomaterials represent an innovative and effective technology for the removal of As in various water and soil matrices, with significant advantages over traditional methods in terms of efficiency, stability, selectivity, and environmental sustainability. Nevertheless, their large-scale application still faces challenges related to production costs, optimization according to soil or water type, and the evaluation of their ecological impact.

In addition, aspects such as biodegradability, interaction with soil microbiota, and leaching risk must be carefully analyzed to ensure safe and sustainable use. These materials have the potential to transform remediation strategies in agriculture, but their implementation must be accompanied by regulatory frameworks, environmental studies, and socio-economic strategies that ensure their responsible and effective adoption in the long term.

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