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Advances in wastewater remediation using functionalized metallic and semiconductor nanomaterials: A systematic review

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ABSTRACT

The increasing scarcity of water resources has driven the need for innovative solutions for wastewater reclamation using different nanomaterials. The purpose of the research was to establish the progress of wastewater remediation using functionalized metallic and semiconductor nanomaterials. A systematic review was carried out following the preferred reporting items for systematic reviews and meta-analyses (PRISMA) methodology with a search comprised between the years 2010 to 2024, from which 50 scientific articles were selected that met inclusion and exclusion criteria. Magnetic, noble, and chalcogenide metallic nanomaterials, as well as semiconductor nanomaterials, were considered. As an advance it was reported that the most efficient nanomaterial in the recovery of contaminated water is ZnO that when functionalized has high adsorption capacity of several heavy metals ions (Cd^{2+}, Hg^{2+} and Pb^{2+}), being reusable for several cycles; for its part, functionalized CuO is highly efficient in the adsorption of Ni^{2+} and Cd^{2+} having an efficiency of 99.16%; another advance found is the use of magnetic nanoparticles Fe_3O_4 and Fe_2O_3 for specific adsorption of heavy metal ions with efficiencies above 99%, and with significant reusability with magnetic desorption methods; for adsorption of dyes and colorants the compound $CoFe_2O_4$ reaches efficiencies of 98.6% for methylene blue and 95.3% for rhodamine B; semiconducting nanomaterials such as TiO_2 stand out in the degradation of organic pollutants by photocatalysis, managing to remove up to 95% of dyes and pesticides; finally, advanced functionalization techniques, such as the use of L-cysteine in Au nanoparticles, have enabled the rapid detection of heavy metals through color changes in plasmons. It is concluded that these advances not only improve efficiency in the remediation of water contaminated by heavy metals, dyes, colorants, and organic and inorganic pollutants in general but also promote sustainability through the repeated use of nanomaterials, which reduces costs and minimizes environmental impact.

Keywords: wastewater remediation, functionalized nanomaterials, adsorption, photocatalysis, nanoparticle toxicity.

INTRODUCTION

Wastewater has multiple origins, mainly coming from anthropogenic sources, such as domestic discharges containing organic matter, detergents, and chemicals; industrial emissions from chemical, metallurgical, and textile sectors, which release heavy metals, organic compounds, and dyes; and agricultural and livestock activities, which pollute with fertilizers, pesticides, and animal waste (Alengebawy et al., 2021). Mining activities are considered the most polluting, generating acidic water drainage and releasing toxic metals such as arsenic and mercury (Mishra et al., 2018). Also, sanitary and hospital wastewater contains pharmaceuticals and pathogens, while urban areas contribute chemical and biological wastes through inefficient drainage systems (Lütterbeck et al., 2020). These pollutants deteriorate water quality, damage aquatic ecosystems, and endanger the health of the population. Although conventional technologies, such as coagulation-flocculation, ion exchange, and filtration, have been used for decades, their effectiveness is limited against complex or emerging pollutants. In this context of improving the treatment of pollutants, applications of metallic and semiconductor nanomaterials emerge as a developing technology that offers solutions with different methods for wastewater remediation (Gour et al., 2024; Tanweer et al., 2024).

Metallic and semiconductor nanomaterials are produced by physical, chemical, and biological methods. Physical methods include laser ablation (Gentile et al., 2021; Naharuddin et al., 2022), evaporation-condensation, and mechanical milling, which reduce particle size by high-energy techniques. Chemical methods, such as chemical reduction, sol-gel, and controlled precipitation (Lian et al., 2020), employ reagents to form stable metal nanoparticles from metal ions. Biological methods, such as biosynthesis and green synthesis, use microorganisms or plant extracts as reducing agents, offering a more environmentally friendly and sustainable option (Agustina et al., 2020; Huston et al., 2021). These nanomaterials are considered suitable for wastewater treatment due to their high surface-to-volume ratio, chemical reactivity, and selective adsorption capacity. They are classified into various categories according to their composition and structure. Pure metal nanoparticles, such as gold (AuNPs) and silver (AgNPs) nanoparticles, are noted for their catalytic and antimicrobial properties (Hossain et al., 2024; Sarfraz and Khan, 2021). On the other hand, metal oxides, such as Fe_3O_4, ZnO, and semiconducting TiO_2, are used in adsorption and photocatalysis processes, being highly effective in the removal of organic pollutants and heavy metals (Ismail et al., 2024; McIntyre and Hart, 2021). In addition, hybrid nanocomposites, such as $AuFe_3O_4$, combine metallic materials with additional components to increase their stability and functionality (Tao et al., 2020).

To enhance the adsorption capacity of contaminants and improve their efficiency, metallic nanomaterials are functionalized. This process involves modifying the surface of nanomaterials by incorporating specific ligands or coatings that improve their adsorption capacity, selectivity, and stability (Khoramian et al., 2024). Among the most common methods encountered is functionalization with inorganic oxides, such as SiO_2, which increases chemical stability and improves interaction with metal contaminants (Ismail et al., 2024). Another approach is the incorporation of organic ligands, such as L-cysteine, which facilitates the detection and selective removal of heavy metals (Khamcharoen et al., 2022; Zhang et al., 2021). Likewise, hybrid coatings combining organic and inorganic materials are effective in multifunctional applications (Salih et al., 2024). Finally, chemical surface modifications, through the incorporation of amino, carboxyl, or sulfhydryl groups, enhance the affinity of the nanomaterial towards specific contaminants, significantly increasing its effectiveness in remediation processes (Chen et al., 2016).

The preferred reporting items for systematic reviews and meta-analyses (PRISMA) methodology is widely recognized for its rigor in the synthesis of scientific information. This methodology allows a transparent and reproducible approach to the analysis of relevant data, ensuring that the findings are based on solid evidence (Moher et al., 2009; Sarkis-Onofre et al., 2021). In this review, the objectives were clearly defined, focusing on advances in wastewater remediation using functionalized metallic and semiconductor nanomaterials. The literature search was carried out in high-impact databases, such as Scopus, Web of Science, and ScienceDirect, covering publications on fixed dates. Inclusion and exclusion criteria were established to select relevant studies, considering variables such as type of nanomaterial, efficiency in the elimination of contaminants, reusability, among others.

The objective of this systematic review was to establish the advances in the recovery of wastewater using functionalized metallic nanomaterials and semiconductors, providing a comprehensive view of the metallic nanomaterials that have the greatest incidence in the recovery of contaminated water, the materials or ligands most used in functionalization and the contaminants from which wastewater can be recovered. The following questions must be answered: 1. Which metallic nanomaterials and functionalized semiconductors have the greatest efficiency in the recovery of contaminated water and what is their reuse cycle? What are the most recurrent pollutants in wastewater? and 3. What are the advances in wastewater recovery with metallic nanomaterials and functionalized semiconductors?

METHODS

Synthesis of nanoparticles

Nanoparticle synthesis can be obtained from two main approaches: top-down and bottom-up, which differ in the starting principle for the creation of nanoparticles (Figure 1). The top-down approach involves the fragmentation of bulk materials into smaller particles until the desired nanometer size is reached (Lu et al., 2016). The methods employed within this approach are usually physical and include techniques such as laser ablation which uses laser pulses to vaporize a solid material, generating nanoparticles in different media such as liquids (Qayyum et al., 2019). Chemical etching and sputtering, employ chemical or physical processes to erode the material and form nanoparticles (Hao et al., 2022). Mechanical-chemical processes combine mechanical forces and chemical reactions. Electric wire explosion: consists of generating nanoparticles by controlled explosion of a metal wire in an inert or reactive medium (Pervikov, 2021). Aerosol-based techniques generate nanoparticles from liquid or solid precursors suspended in a gas (Gautam et al., 2021).

Whereas, the bottom-up approach builds nanoparticles from atoms or molecules, forming aggregates that are organized into clusters and subsequently into nanometer particles (Lin et al., 2022). Methods within this approach include the chemical method, where chemical vapor deposition occurs where gaseous precursors decompose to form a layer of the desired material. The chemical reduction method employs reducing agents to synthesize nanoparticles from metal ions, where ion exchange reactions, generate nanoparticles by ion transfer between compounds (Szczyglewska et al., 2023). On the other hand, the biological method is green synthesis which uses living organisms such as bacteria or fungi to synthesize

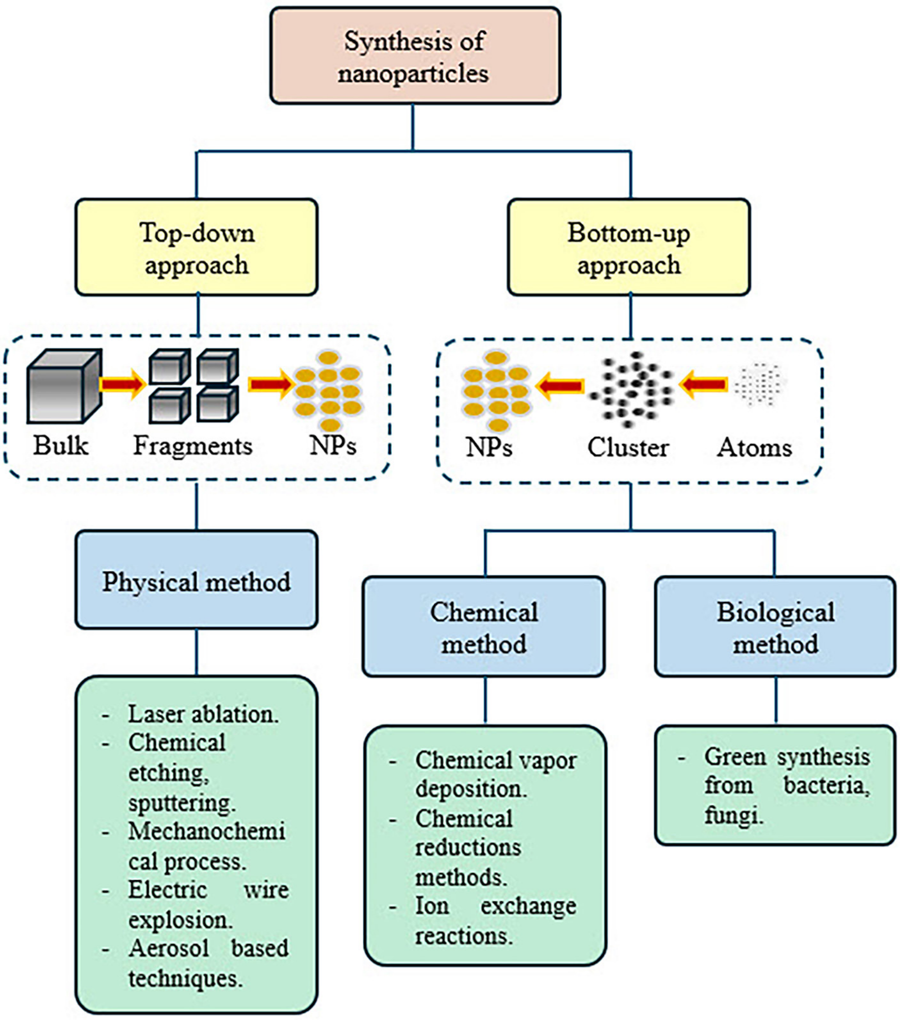

Figure 1. Diagram of top-down and button-up approaches for nanoparticle synthesis

nanoparticles in an environmentally friendly manner (Hirschi et al., 2022).

Classification of metallic and semiconductor nanoparticles

Metallic and semiconducting nanoparticles exhibit diverse characteristics according to their phase composition and material type. From Figure 2, metallic nanoparticles fall into three main categories, each with unique properties that make them highly effective in the treatment of contaminated water. Magnetic nanoparticles (Fe_2O_3, Fe_3O_4) are notable for their response to magnetic fields, which facilitates the adsorption and removal of heavy metals and organic pollutants through efficient separation processes (Rawat et al., 2023). Noble metal nanoparticles (Au, Ag, Pt), recognized for their optical and catalytic properties, are used in the detection of heavy metals through changes in their optical properties, as in the case of L-cysteine functionalized AuNPs (Zhang et al., 2021; Zhao et al., 2020). Semiconducting nanoparticles (ZnO, SiO_2, TiO_2) are essential in photocatalysis processes, taking advantage of UV radiation to decompose organic pollutants and toxic species (Ghamarpoor et al., 2024). Finally, metal chalcogenides (PbS, ZnS, CdS, ZnSe, CdTe, HgS) possess photochemical and electronic properties that make them ideal for photocatalysis and specific detection of pollutants (Madkour et al., 2021).

Most widely used nanoparticle functionalization techniques

The surface functionalization of metallic nanoparticles, by different methods, allows for modifying their physicochemical properties and optimizes their performance in different applications, as is the case of wastewater treatment. Figure 3, presents the different functionalization methods or techniques: functionalization with thiolated surfactants, where molecules with thiol groups (-SH) form stable covalent bonds with the

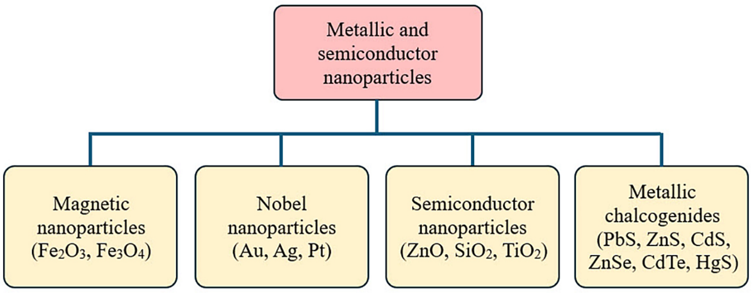

Figure 2. Classification diagram of metallic and semiconducting nanoparticles

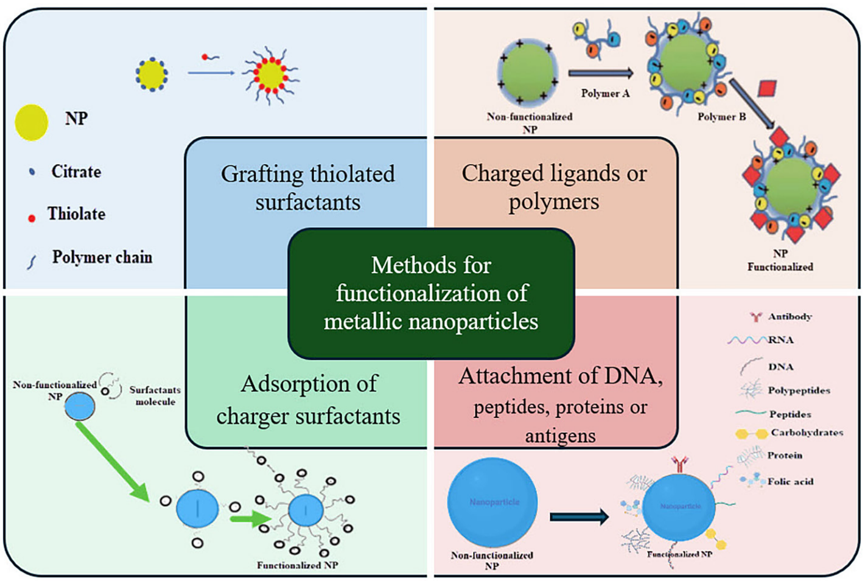

Figure 3. Métodos más utilizados para la funcionalización de nanopartículas metálicas

metal surface, improving colloidal stability and compatibility in various environments (Agarwal and Kumar, 2021). Coating with charged ligands or polymers adjusts stability and prevents aggregation, favoring specific interactions in biological and environmental applications (Agarwal and Kumar, 2021; Madkour et al., 2021). On the other hand, the adsorption of charged surfactants alters surface charge and hydrophobicity, adapting nanoparticles to different media (Khoramian et al., 2024). Finally, the binding of biomolecules such as DNA, peptides, proteins, or antigens provides specificity to interact with biological targets, being important in biomarker detection, targeted therapy, and biosensor development (Paramasivam et al., 2024).

Systematic review of articles

Six keywords were used to search for articles: "metallic nanoparticle functionalized wastewater treatment", "metals nanoparticle functionalized for wastewater treatment", "magnetic nanoparticle functionalized wastewater treatment", "novel nanoparticle functionalized for wastewater treatment", "semiconductor nanoparticle functionalized wastewater treatment" and "chalcogenides nanoparticle functionalized wastewater treatment". The literature reviewed included articles from journals indexed in Scopus databases, including ScienceDirect, Elsevier, SpringerLink, Nature, and others. Studies published from 2010 to 2024, in the English language, that addressed advances in the use of nanomaterials for wastewater treatment were selected. The PRISMA methodology was used to structure and systematize the selection and review of the articles, the sequence of which is illustrated in Figure 4; where, in the Identification stage, 604 records were initially found through searches in academic databases and 4 records from other external sources were added. Of these, 9 records were excluded because they were published before

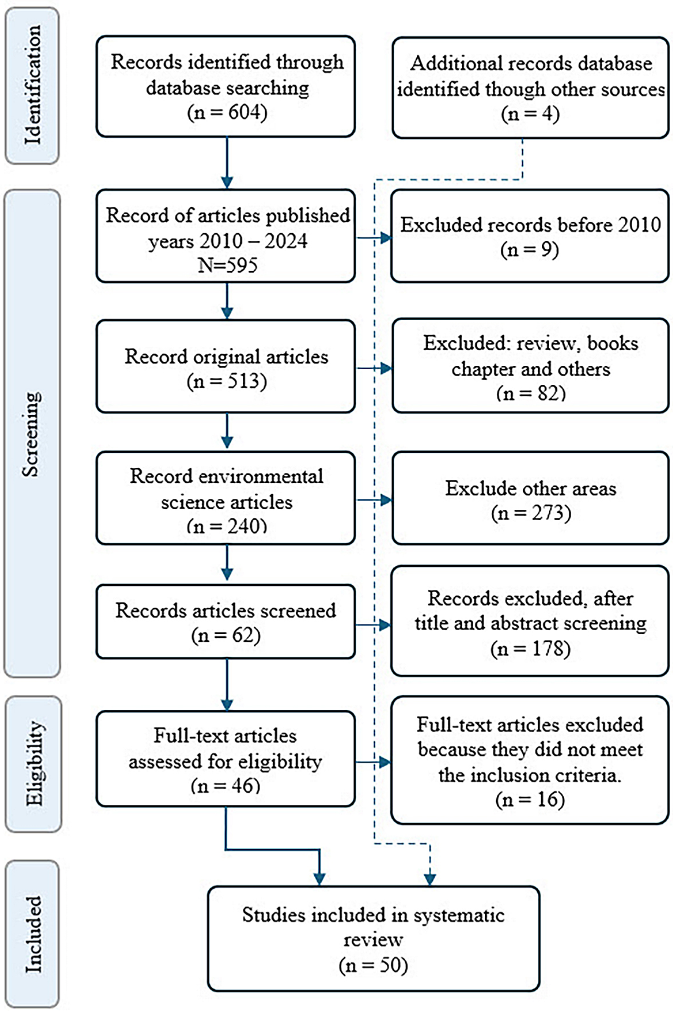

Figure 4. Diagram of the methodology followed for the systematic review and meta-analysis (PRISMA)

2010, which did not meet the temporal criteria. In the screening stage, the remaining 595 articles, published between 2010 and 2024, were evaluated for relevance; during this phase, 82 articles were excluded because they were reviews, book chapters, and other types of non-original publications, which were not in accordance with the review criteria. In addition, 273 records were discarded for not belonging to the area of environmental sciences, which reduced the sample to 240 articles that covered the central theme of the research. In the eligibility stage, 62 articles were selected and evaluated in full text to verify whether they met the specific inclusion criteria of the review; at this point, 16 articles were excluded for not meeting the established requirements, which allowed further refining of the selection. Finally, in the inclusion stage, 50 studies were considered in the systematic review, for the analysis of wastewater recovery using functionalized metallic and semiconductor nanomaterials

Bibliometric analysis

The bibliometric analysis was carried out with the VOSviewer software (Donthu et al., 2021), which allowed the processing of the selected articles and obtaining a global view of the trends of the object under investigation. Figure 5 represents the co-occurrence network map generated with VOSviewer, which shows the relationships between keywords in research on wastewater remediation using functionalized nanomaterials. The most prominent terms, such as *wastewater treatment*, *adsorption*, *metal nanoparticles,* and *heavy metals*, reflect their centrality in the field, while the different thematic clusters identified (red, green, and blue) group specific aspects of the topic. The red cluster focuses on adsorption and reaction kinetics, fundamental for evaluating the interaction between nanomaterials and contaminants, while the green cluster highlights material characterization and functionalization techniques, essential for improving treatment efficiency. The blue cluster addresses chemical synthesis and practical applications, such as the removal of dyes and aromatic compounds. Dense connections between terms such as *adsorption* and *wastewater treatment* highlight the relevance of process optimization, while mentions of secondary terms, such as *membranes* and *reusability*, underline the growing importance of sustainable and reusable approaches.

From the main keywords of the co-occurrences presented in Table 1, it is confirmed that *"Adsorption"* and "*Wastewater treatment"* have the highest occurrences and link strengths (426 and 352, respectively), reflecting their relevance in the development of decontamination solutions. In addition, materials functionalization and chemical approaches, represented by terms such as *"Functionalized"* and *"Chemistry"*, stand out as key strategies in the research work. The importance of nanomaterials is evident with words such as *"Magnetite"*, *"Nanomagnetics",* and

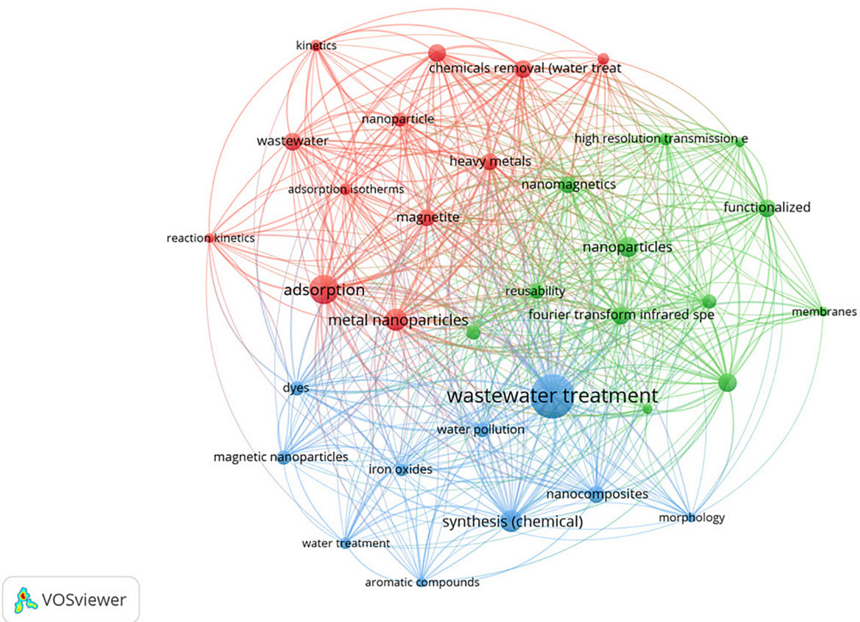

Figure 5. Map of Co-occurrence Networks

Table 1. Primary Co-occurrences of keywords

Keyword	Occurrences	Total link strength
Adsorption	50	426
Wastewater treatment	52	352
Wastewater	28	269
Functionalized	32	266
Chemistry	22	260
Magnetite	26	247
Water pollutant	17	220
Magnetism	18	211
Waste water	18	188
Nanomagnetics	19	176
Nanoparticle	18	176
Waste water management	15	168
Silicon dioxide	12	163
Silica	17	160
Nanoparticles	20	151
Synthesis	12	151
Nanocomposite	12	137
Metal ions	18	136
Nanocomposites	14	132
Desorption	12	129
Heavy metals	14	109
Metal nanoparticles	12	41

"Nanocomposites", highlighting the role of magnetic and structural properties in the separation and recovery of pollutants, especially heavy metals, as indicated by *"Heavy metals"* and *"Metal ions"*. Likewise, concepts such as *"Water pollutant"* and *"Desorption"* show an interest in the mitigation and recovery of specific pollutants, while the presence of terms related to materials such as *"Silica"* and *"Silicon dioxide"* suggests their use in adsorbent applications.

RESULTS

To answer the questions: (1) Which functionalized metallic and semiconductor nanomaterials have the highest efficiency in the recovery of contaminated water and what is their reuse cycle?, (2) Which contaminants are the most recurrent in wastewater?, and (3) What are the advances in the recovery of wastewater with functionalized metallic and semiconductor nanomaterials? The information was systematized considering the nanomaterial (NM), functionalization method, applications, efficiency, and reuse cycle, which are presented in Table 2. With the data from the articles selected and systematized in Table 2, using the PRISMA methodology, once the meta-analysis had been carried out, we proceeded to answer the questions posed. In response to question 1; the most efficient functionalized metallic and semiconductor nanomaterials in the remediation of contaminated water are ZnO, which combines high efficiency (over 85% for adsorption of Cd^{2+}, Hg^{2+} and Pb^{2+}) with the highest reuse cycle (eight cycles) (Tanweer et al., 2024), and Fe_3O_4, with up to 99% efficiency for heavy metal removal and six-cycle reuse (Ismail et al., 2024). $CoFe_2O_4$ also stands out, reaching efficiencies of 98.6% for methylene blue and 95.3% for rhodamine B, with a reuse cycle of five times (Salih et al., 2024). For its part, functionalized CuO is highly effective in adsorbing Ni^{2+} and Cd^{2+} (99.16%), although its reuse cycle is limited to a single use due to its high reactivity (Bahjat Kareem et al., 2024). Finally, the semiconducting nanoparticle TiO_2 shows efficiencies of 83% to 95% in the degradation of organic pollutants and can be reused multiple times in photocatalytic processes (McIntyre and Hart, 2021).

In response to question 2; the most recurrent pollutants in wastewater are heavy metals such as lead (Pb^{2+}), cadmium (Cd^{2+}), and mercury (Hg^{2+}), present in industrial and mining effluents (Ismail et al., 2024; Tanweer et al., 2024). Secondly, industrial dyes such as methylene blue (MB) and rhodamine B (RhB), derived from textile activities and other industries, stand out (Salih et al., 2024). Third, organic pollutants, such as pesticides, proteins, polysaccharides, and pharmaceutical compounds, are frequent in agricultural, urban, and sanitary discharges (Jassim et al., 2024; McIntyre and Hart, 2021). Finally, there are specific chemical residues such as caffeine and nitrophenols that are detected in sanitary and industrial effluents (Franzoso et al., 2017; Hou et al., 2020).

In response to question 3; advances in wastewater remediation using metal nanomaterials and functionalized semiconductors include high adsorption capacity, such as that of Fe_3O_4, reaching up to 882.76 mg/g for Pb^{2+}, and ZnO, with 840.33 mg/g for Cd^{2+} (Ismail et al., 2024; Tanweer et al., 2024). In addition, semiconductors such as TiO_2 excel in the degradation of organic pollutants by photocatalysis, managing to remove up to 95% of dyes and pesticides (McIntyre and Hart, 2021). Multifunctional nanocomposites, such as $CoFe_2O_4$, combine heavy metal and dye removal

Table 2. Nanomaterials, application, efficiency, and reuse cycle

N°	NM	Functionalization method	Molecular compound (functionalized)	Application	Efficiency: Maximum capacity (adsorption/ degradation/ inhibition)	Efficiency: %	Reuse cycles	Ref.
1	Fe_2O_3	Eco-friendly synthesis of magnetic nanoparticles with onion residues functionalized with DL-homocysteine	HC@SiO_2@MNP @OW	Selective adsorption of Hg ions in wastewater	88.5 mg/g	84%	Five	(Gour et al., 2024)
2	ZnO	Intraparticle diffusion model for heavy metal adsorption	ZM-g-Pani	Adsorption of Cd^{2+}, Hg^{2+} and Pb^{2+} ions	840.33 mg/g (Cd^2), 497.51 mg/g (Hg^2), 497.51 mg/g (Pb^2)	> 85%	Eight	(Tanweer et al., 2024)
3	CuO	Hummers method for the preparation of GO/CuO nanocomposites	GO/CuO	Adsorption of heavy metal ions such as Ni^{2++} and Cd^{2++} in wastewater	At pH 8 and 250 mg adsorbent in 15 min	99.16% (Ni^{2++}) and 98.84% (Cd^{2+})	One	(Bahjat Kareem et al., 2024)
4	TiO_2	Membranes were created using the phase inversion method	GO/TiO_2	Hydrophilic adsorption (proteins and polysaccharides) in water	150 kg/hm² to 275 kg/hm²	83% - 92%	N.S.	(Jassim et al., 2024)
5	Fe_3O_4	Synthesis of magnetic silicate core-shell nanocomposites characterized for Cd (II) adsorption	Fe_3O_4@SiO_2	Cd (II) removal in wastewater	32.50 mg/g at pH 8 for Cd (II) for 405 min	86.7% - 99%	Six	(Ismail et al., 2024)
6	$CoFe_2O_4$	Nanoparticle coating with silica functionalized 3-aminopropylethoxy--silane modified with gallic acid for dye removal	MgCF @SiO_2 -NH-COOH	Adsorption of methylene blue and rhodamine B dyes	103 mg/g for MB, and 89 mg/g for RhB	98.6% (MB) 95.3% (RhB)	Five	(Salih et al., 2024)
7	Ag	Solvothermal carbonization of activated rice husks using potassium hydroxide impregnated with silver nanoparticles	A-RI@Ag	Removal of multiple heavy metal ions from wastewater	From 100 - 230 mg/g for Cu^{2++}, from 513 - 569 mg/g for Fe^{3++}, from 164 -190 mg/g for Pb^{2++}, and from 64 and 100 mg/g for Zn^{2++}	N.S.	One	(Hossain et al., 2024)
8	Fe_2O_3	Functionalization of biochar with iron oxide for heavy metal sorption	Fe_2O_3/BC/Mxene	Wastewater treatment to remove lead and methyl blue	882.76 mg/g for Pb^{2+}, and 758.03 mg/g for MB at 293 °K	N.S.	One	(Bukhari et al., 2024)
9	Ti-Cu-Zn	Preplasmonic functionalization of metal-doped graphene oxide nanoparticles	TCZ-GO	Degradation of dyes in wastewater	N.S.	85%	One	(Pandiyaraj et al., 2023)
10	ZnO	Sonication for sample preparation	ZnO-W and ZnO-Sb	Photocatalytic degradation of methylene blue dye from wastewater	300 mg/L and 10 ppm of dye at pH 9.	91%	One	(Modi et al., 2023)
11	Ag	BET analysis for surface area measurement	Mag @AC1 -Ag and Mag @AC2 -Ag	Removal of Pb (II) and Cd (II) from wastewater.	The sorption capacity had the ratio Pb^{2+} > to Cd^{2+}.	N.S.	N.S.	(Ali et al., 2023)
12	Ag	Hydrothermal technique to synthesize dip-coated Ag-CuO nanoparticles to modify ceramic membranes	Ag-CuO	Treatment of oily wastewater using modified ceramic membranes	0.5% by weight membrane achieved 30% higher water flux	97.80%	One	(Avornyo et al., 2023)
13	ZnO	Biodegradation techniques for dye degradation	ZnO/Ag	Degradation of dyes in contaminated water	Degradation of dyes 80 mg /L in 1.5 h	86%	Five	(Vikal et al., 2023)
14	SnO_2	Synthesis of SnO_2 nanoparticles using a green chemistry approach	SnO_2/Ga	Photocatalytic degradation of citalopram in wastewater treatment	25.00 µg/mL) in 1 h using UV light (1.01 mW/cm)²	88.43 ± 0.7%	Three	(Nazim et al., 2023)

15	$nTiO_2$	Respiration inhibition experiments, microorganisms were exposed to various concentrations of nanoparticles	$nTiO_2$/f-MWCNT	Inhibition of respiration in activated sludge and E. coli	In E. coli 100 mg/L, in activated sludge 50 mg/L	36% 24%	One	(Luppi et al., 2022)
16	Au	Functionalization of gold nanoparticles with L-Cysteine	AuNPS/L-Cysteine	Detection of metals in contaminated water by color	>500 uM (Cd^{2+}, Pb^{2+} y As^{3+})	N.S.	N.S.	(Carbajal-Morán et al., 2022)
17	$AuFe_3O_4$	Functionalization of multi-walled carbon nanotubes with acids and iron oxide and gold nanoparticles with green tea extract	MWCNT-Au/Fe_3O_4	Removal of Pb ions^{2+} from synthetic wastewater	7,266 mg/g at 298 °K	78%	N. S.	(Tao et al., 2020)
18	Ag	Sonochemical approach to synthesize Ag@HAp nanostructures	consortia/Ag @ Hap	Wastewater treatment	Consortia 5ppm	95%	N. S.	(Rajendran et al., 2022)
19	Fe_3O_4	Synthesis and characterization of magnetite nanoparticles	Fe_3O_4/C_24H_51OP	Removal of toxic metal ions from wastewater	14 mg/g for Ni^{2+} and Cd^{2+} in synthetic wastewater		One	(Ali et al., 2022)
20	Fe_3O_4	Functionalization of biochar with Fe particles O_{34} at the nanoscale	PS-Fe_3O_4	Removal of Pb(II) ions from garden wastewater	188.68 mg/ g	>71.86%	Four	(Jin et al., 2022)
21	$MnCo_2O_4$	Synthesis of $MnCO_2O_4$ nanomaterials by X-ray diffraction	PSF-$MnCo_2O_4$	Wastewater treatment using nanostructured polymeric membranes	N.S.	99.86% (Congo red) and 99.81% (humic acid).	N.S.	(Chandra et al., 2022)
22	Fe_3O_4	Functionalization of magnetic chitosan microparticles with aminothiazole and imidazole carboxamide	AIC@MC	Treatment of tannery wastewater	6 mmol Cr (IV)/g	>99%	Five	(Hamza et al., 2022)
23	Fe_3O_4	Chemical fabrication of MoF/NH_2/Fe_3O_4 composites and Fe_3O_4 magnetic nanoparticles by the solvothermal method	MoF/NH_2/Fe_3O_4	Potential adsorbent for industrial wastewater treatment	618 mg/g	>90%	Six	(Alzahrani et al., 2022)
24	TiO_2	Functionalization of TiO_2 nanoparticles with collagen for water remediation	TiO -$APTES_2$	Remediation of organic dyes from wastewater	High degradation of RhB under visible light irradiation in 130 min	> 73%	Two	(Nagaraj et al., 2021)
25	SiO_2	Chemical modification of mesoporous silica nanoparticles	MSN/PSU	Removal of heavy metal ions from wastewater	High cadmium and zinc removal efficiency	> 90%	One	(Alotaibi et al., 2021)
26	TiO_2	Functionalization of TiO_2 nanoparticles that adhere to cement for treatment of organic contaminants	TiO_2/MAH	Treatment of organic pollutants in rainwater	Elimination of methylene blue	> 95%	Multiple	(McIntyre and Hart, 2021)
27	SiO_2	Functionalization of silica solidity for the treatment of acid mine drainage	SSOD/HNO_3/ H_2SO_4	Removal of heavy metals from wastewater	The 10% FSSOD/ PSF membrane achieved rejection of Fe^{3+}, Ca^{2+}, Mn^{2+}, Mg^{2+} and Na^{2+} at 4 bar	> 50%	Multiple	(Ntshangase et al., 2021)
28	SiO_2	Preparation of magnetic core and shell nanoparticles for dye removal	MNP@PAAA-FA	Removal of crystal violet dye from wastewater	19.45 mg/g	> 88.74%	Ten	(Ganea et al., 2021)
29	$CoFe_2O_4$	Synthesis of CBCM nanocomposites using $CoFe_2O_4$ and CB	CBCM	Removal of cationic dyes from wastewater	199.20 mg/g (CV), 78.31 mg/g (MB) and 55.62 mg/g (RhB)	N. S.	Multiple	(Kanth P et al., 2021)
30	Fe-O	Synthesization of graphene oxide modified soda-lime glass composite for water purification	GO-SLS	Removal of arsenic (As (V)) from groundwater	708 mg/g	> 72%	Multiple	(Mandal et al., 2021)
31	Fe_3O_4 and Fe_2O_3	Coprecipitation method to synthesize IONP and UV action for MB adsorption	IONP	Elimination of organic dyes in water generated in the pharmaceutical industry	High adsorption of MB with IONP incubated with K ions	> 50%	Five	(Singh et al., 2020)

32	$FeCl_3$, and $FeSo_4$	Leaves of C. dactylon and M. koenigii were collected and processed, and Cr (VI) stock solution was prepared using $K_2Cr_2O_7$	AF-MnP-L1, AF-MnP-L2	Removal of chromium (VI) metal contaminants from wastewater	34.7 mg/g	> 96,36%	Five	(Vishnu and Dhand--apani, 2020)
33	Al_2O_3	Synthesis of PVA/SA beads using glutaraldehyde as a crosslinking agent	Zeo/PVA/SA	Removal of heavy metals from wastewater	99.5% for Pb^{2+}, 99.2% for Cd^{2+}, 97.2% for Cu^{2+}	60% - 99.8%	Ten	(Isawi, 2020)
34	TiO_2	Direct sol-gel electrospinning of dip-coated silica sol-gel for TiO_2 functionalization	TiO_2/SNM	Elimination of pesticides in water	5 and 10 mg/L in < 8 h for isoproturon	> 90%	Five	(Loccufier et al., 2020)
35	Fe_3O_4	Development of magnetic nanocomposites with polyacrylic acid and cellulose with adsorption analysis using Langmuir and Freundlich isotherm models	Fe_3O_4@Si-NH_2	Removal of cationic dyes from aqueous solutions	332 mg/g for methylene blue	> 68%	Five	(Samadder et al., 2020)
36	TiO_2	Synthesis of PDMS particles by oil-in-water emulsion with incorporation of MWCNTS/TiO_2 nanocomposites	MWCNTS/TiO_2	Treatment of wastewater contaminated with azo dyes	19 mg/L	> 70%	Three	(Lian et al., 2020)
37	$CuFe_2O_4$/Ag	Magnetic synthesis of $CuFe_2O_4$ /Ag nanoparticles via polydopamine reduction	$CuFe_2O_4$/Ag@COF	Nitrophenolic wastewater treatment	Not specified	> 95%	Six	(Hou et al., 2020)
38	Fe_3O_4	Solvothermal process to synthesize MNP	Fe_3O_4@PEI	Heavy metal wastewater treatment	60.98 mg/g in 5 min	N.S.	Five	(Tao et al., 2020)
39	CuO	Development of functionalized CuO nanoparticles for dye adsorption	CuO@EDTA	Treatment of water pollution caused by industrial dyes	N. S.	> 54%	N.S.	(Geetha et al., 2020)
40	Fe_3O_4	Synthesis of magnetic graphene oxide and Fe_3O_4@SiO_2	Fe O @SiO_{342} -NH-SH and MGO-NH-SH	Removal of mercury ions (II)	MGO-NH-SH is more efficient in removing Hg from water than Fe_3O_4 @SiO -NH-SH.	> 60%	Ten	(Kazemi et al., 2019)
41	Fe_3O_4	Digestion and oxidation of NPs to determine thiol groups with ultrafiltration to separate free and bound DMSA	IONP @ DMSA	Evaluation of the environmental stability of DMSA-coated IONPs	DMSA-coated IONPs show long-term environmental stability	> 60%	N.S.	(Bemowsky et al., 2019)
42	Fe_3O_4	Synthesis of Fe nanoparticles O @ SiO_{342} @PEI -NTDA and evaluation of heavy metal ion adsorption performance	Fe O_{34} @SiO_2 @ PEI -NTDA	Removal of Pb ions^{2+} in contaminated water	285.3 mg/g	N.S.	Six	(Jia et al., 2019)
43	Fe_3O_4	Synthesis of imine-functionalized magnetic nanoparticles	Fe O @SiO @ PEI-$NTDA_{342}$	Removal of toxic metal ions from aqueous solutions	54.53 mg/g for Zn^{2+}, 57.60 mg/g for As^{3+}.	N.S.	Six	(Ojemaye et al., 2018)
44	PMNP/F. chinensis Roxb.	Obtaining phytogenic magnetic nanoparticles functionalized with 3-mercaptopropionic acid	3-MPA@PMNPS	Removal of cationic dyes from textile wastewater	81.2 mg/g at pH 6 to 12 in 120 min	> 85%	Five	(Ali et al., 2018)
45	Ag	Electrospinning for the manufacture of heat-treated membranes for the preparation of composites	PVA/PAA/GO-COOH@AgNPs	Treatment of wastewater containing dyes by photocatalysis	25 mg/g	N.S.	Eight	(Liu et al., 2018)
46	$FeCl_3$ and $FeSO_4$	Fenton-like and photofenton-like caffeine degradation experiments with magnetic nanoparticles	$FeCl_3$ - $FeSO_4$ stabilized with BBS.	Degradation of caffeine in magnet-sensitive heterogeneous processes to remove contaminants	1 mg/L in 60 min with photochemical treatment	95%	N.S.	(Franzoso et al., 2017)
47	Fe_3O_4	Use of lysis enzymes coupled to magnetic nanoparticles for Mycobacterium tuberculosis capture by specific antibodies	NP-NH -$antibody_2$	Treatment of wastewater contaminated with Mycobacterium tuberculosis	The optimum reaction time for catalytic productivity was 30 minutes.	88%	N.S.	(Nguyen et al., 2016)

48	Fe_3O_4	Single-vessel synthesis of amino-functionalized magnetic nanoparticles	Fe_3O_4 -NH_2	Wastewater treatment for heavy metal detection	232.51 mg/g for Cr (VI)	96%	N.S.	(Baghani et al., 2016)
49	Fe_3O_4	Coating of Fe nanoparticles O_{34} with APTES	Fe O_{34} @SiO_2 -NH-HCG.	Removal of heavy metal ions from wastewater	The removal efficiency of any Fe_3O_4 @ SiO_2 - NH - HCG is greater than 96% in 20 min.	> 67%	Eleven	(Chen et al., 2016)
50	Fe_3O_4	Functionalization of biomagnetite nanoparticles with 3-mercaptopropionic acid mixed by ultrasound	3 MPA @Fe_3O_4	Removal of Ni(II) from aqueous solutions	42.01 mg/g at pH 6.	> 75%	Five	(Venkates- -warlu et al., 2015)

Note: APTES – 3-Aminopropyltriethoxysilane, BC – biochar, FA – folic acid, GO – graphene oxide, PAAA – polyacrylic acid, Pani – polyaniline, PEI – polyethylenimine, PSU – polysulfone, MNP – magnetic nanoparticles, MWCNT – multi-walled carbon nanotubes, N.S. = not specified.

with efficiencies above 98% for methylene blue (Salih et al., 2024). Sustainability has also improved significantly, with materials such as ZnO and Fe_3O_4 that can be reused for up to eight and six cycles, respectively, without noticeable loss of efficiency (Ismail et al., 2024; Tanweer et al., 2024). Finally, advanced functionalization techniques, such as the use of L-cysteine on AuNPs, have enabled the rapid detection of heavy metals through color changes (Carbajal-Morán et al., 2022).

CONCLUSIONS

In this work, a systematic review of 50 studies using PRISMA methodology was carried out on the most recent advances in wastewater remediation using metallic nanomaterials and functionalized semiconductors. From the results obtained, functionalized metallic and semiconductor nanomaterials, such as ZnO, Fe_3O_4, $CoFe_2O_4$, CuO and TiO_2, have a high capacity for adsorption and degradation of pollutants, with high efficiencies, firstly for the removal of heavy metals, such as lead (Pb^{2+}), cadmium (Cd^{2+}) and mercury (Hg^{2+}), and secondly organic pollutants such as dyes and pesticides. Among the most significant advances, ZnO stands out for its combination of high efficiency (over 85% for heavy metal adsorption) and its longer reuse cycle (up to eight cycles), while Fe_3O_4 shows an adsorption capacity of up to 882.76 mg/g for Pb^{2+} and a reuse of six cycles. In addition, TiO_2 stands out for its photocatalytic capacity to degrade organic pollutants under visible and ultraviolet light, achieving efficiencies above 95%.

These advances not only improve remediation efficiency, but also promote sustainability through the repeated use of nanomaterials, which reduces costs and minimizes environmental impact. Functionalization of these nanomaterials has improved their properties, increasing selectivity and contaminant removal efficiency. Despite the advances, challenges remain, such as the optimization of the reuse cycles of certain nanomaterials and the need for more efficient functionalization techniques for the treatment of specific pollutants.

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