

Review

Silver Nanoparticle-Based Hybrid Nanomaterials for Monitoring and Treatment of Hospital Wastewater: Focus on Rare Earth Elements and Radiopharmaceutical Residues from Nuclear Medicine Department

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Featured Application

Silver nanoparticle-based hybrid nanomaterials can be applied for the monitoring, adsorption, separation, and photocatalytic treatment of hospital wastewater, with a focus on contamination by rare earth elements and radiopharmaceutical residues, contributing to the development of advanced technologies for nuclear medicine wastewater management and environmental protection.

Abstract

Hospital wastewater has begun to act as an important source of emerging contaminants, including rare earth elements (REEs), mostly lanthanides, and radiopharmaceutical residues originating from diagnostic and therapeutic nuclear medicine procedures. The increasing use of gadolinium-based contrast agents, lutetium-containing therapeutics, technetium-99m tracers, iodine-131, yttrium-90, and gallium-68 radiopharmaceuticals has raised growing concerns regarding the release of radioactive and metal-containing compounds into aquatic environments. Conventional wastewater treatment plants are often inefficient in removing these contaminants because of their high chemical stability, low environmental concentrations, and complex aqueous speciation. In this context, hybrid nanomaterials containing silver nanoparticles (AgNPs) have attracted increasing interest for both monitoring and remediation applications. AgNP-based systems exhibit unique plasmonic, catalytic, antimicrobial, and sensing properties that can be exploited in adsorption, photocatalysis, membrane filtration, electrochemical detection, and surface-enhanced Raman spectroscopy (SERS). This review critically analyzes recent advances in hospital wastewater treatment and how hybrid nanomaterials containing silver nanoparticles (AgNPs) are emerging. The review places a particular focus on contamination by REEs and radiopharmaceuticals residues, which to date, as far as we know, remains a challenging and understudied aspect, as reflected by limited publications.

Keywords: hospital wastewater; rare earth elements; radiopharmaceuticals; silver nanoparticles; nanocomposites; hybrid nanosystems

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1. Introduction

Hospital effluents are no longer regarded only as microbiologically contaminated wastewater streams; they are now recognized as chemically diverse point sources of emerging contaminants entering municipal sewer networks and, ultimately, aquatic environments [1–6]. Their composition is shaped by clinical practice and may include disinfectants, antibiotics, analgesics, cytostatic agents, antibiotic-resistant bacteria, antimicrobial resistance genes, pathogens, imaging agents, and residues from nuclear medicine. Within this broad contaminant profile, metal-containing diagnostic agents and medical radionuclides deserve specific attention because they combine high environmental persistence with analytical and regulatory complexity.

The environmental relevance of rare earth elements (REEs) in hospital wastewater is closely linked to the intensive use of magnetic resonance imaging (MRI) by means of gadolinium (Gd), while radiopharmaceutical residues come from diagnostic and therapeutic systems that exploit radiometals such as ^{99m}Tc , ^{131}I , ^{177}Lu , ^{90}Y , ^{68}Ga , ^{111}In , and ^{223}Ra .

Gadolinium-based contrast agents (GBCAs) are designed to remain highly soluble and kinetically inert during clinical use; after administration, however, a large fraction is excreted and can reach wastewater treatment plants. Their stability, which is essential for patient safety, also limits removal during conventional treatment and explains the frequent detection of anthropogenic Gd anomalies in wastewater, surface waters, and drinking-water-related systems [7–15].

In parallel, diagnostic and therapeutic radiopharmaceuticals may introduce radionuclides such as ^{99m}Tc , ^{131}I , ^{177}Lu , ^{90}Y , ^{68}Ga , ^{111}In , and ^{223}Ra into hospital sewage following administration, excretion, or decontamination operations [16–23].

These contaminants are problematic because standard wastewater treatment processes were not developed to manage radiochemical speciation, metal–chelate persistence, or ultra-trace lanthanide concentrations. Activated sludge, sedimentation, and conventional disinfection may reduce organic load and pathogens, but they are not selective for GBCAs, iodide/iodate species, radiometal complexes, or stable lanthanide-containing molecules [4,16,17,24,25]. Consequently, research is moving toward advanced materials able to combine separation, degradation, sensing, and recovery within modular treatment schemes.

Nanotechnology offers useful design opportunities in this context. Nanoscale materials provide high interfacial area, adjustable surface chemistry, optical responsiveness, redox activity, and compatibility with membranes, carbonaceous matrices, oxides, hydrogels, and magnetic supports. Silver nanoparticles (AgNPs) are particularly attractive because their localized surface plasmon resonance, antimicrobial action, catalytic activity, and surface functionalization capacity can be exploited for both monitoring and treatment [26–34].

Based on the Scopus analysis, “hospital wastewater” has become a well-established and steadily growing field with more than 1600 English-language articles and reviews published between 2020 and 2025. Annual publication outputs remained consistently high, peaking in 2024, reflecting the increasing scientific and societal concern regarding contaminants released from healthcare facilities.

The literature, in the 2020–2026 range, contains 310 studies investigating the use of “silver nanoparticles” (AgNPs) for the treatment of hospital wastewater systems.

However, despite this substantial body of literature, topics related to “rare earth elements” (REEs) and “radiopharmaceutical” remain unexplored. A total of 10 publications (<0.7% of the total dataset regarding “hospital wastewater”) mention rare earth elements, while only 6 publications (<0.4% of the same total dataset) address radiopharmaceuticals (see Figure 1). Even trying to broaden the research to a time interval of 15 years, which is between 2011 and 2026, we find on SCOPUS 3466 articles and reviews in English on hospital wastewater, but among these there are still very few referring to REEs (126 works) or radiopharmaceutical residues (18 works). These findings reveal a significant

knowledge gap, particularly considering the growing use of REE-based radionuclides in modern nuclear medicine and targeted radiotherapy. The limited number of studies suggests that the occurrence, monitoring, environmental fate, and recovery of these emerging contaminants from hospital effluents have not yet received adequate scientific attention.

Consequently, the intersection between hospital wastewater management, radiopharmaceutical contamination, rare earth element recovery, and nanotechnology-based treatment approaches represents a highly promising and largely untapped research area. Future studies focusing on the development of selective nanomaterial-based platforms for the detection, removal, and recovery of REE-containing radiopharmaceutical residues could provide both environmental and economic benefits while addressing emerging challenges associated with sustainable healthcare practices and critical raw material recovery.

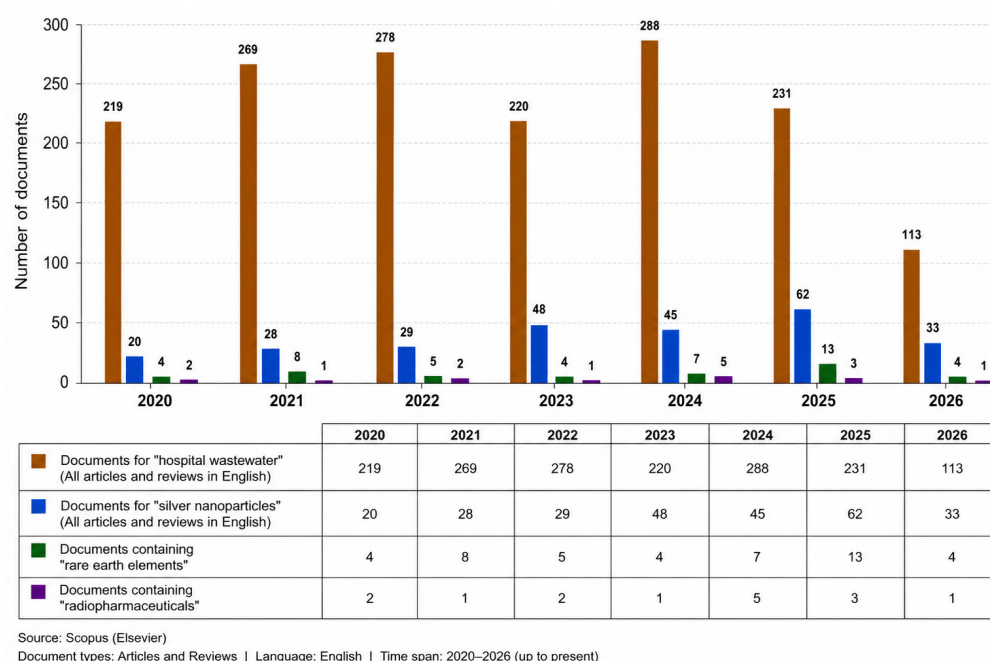


Figure 1. Annual number of Scopus-indexed English-language articles and reviews related to “hospital wastewater” published between 2020 and 2026 (up to the present), and the subset of documents containing the words “silver nanoparticles”, “rare earth elements”, or “radiopharmaceuticals”. Data source: Scopus (Elsevier). Time span: 2020–2026 (up to June 2026).

In this context, we propose this review, collecting the most up-to-date and cutting-edge works, both on hospital water pollution, with a focus on rare earth elements and radiopharmaceutical residues, and on silver nanoparticles, which are used in various fields for water treatment (detection, degradation, and antimicrobial activity) and are proving promising even in this specific and underdeveloped sector.

2. Hospital Wastewater

Hospital wastewater represents one of the most complex anthropogenic aquatic matrices due to the simultaneous presence of pharmaceuticals, disinfectants, contrast agents, radionuclides, pathogenic microorganisms, antibiotic-resistant bacteria, and a wide variety of organic and inorganic contaminants. Unlike municipal wastewater, hospital effluents are characterized by highly variable composition, intermittent contaminant discharge patterns, and the occurrence of compounds specifically associated with medical activities.

The complexity of hospital wastewater is further increased by the coexistence of contaminants exhibiting markedly different physicochemical properties. Organic pollutants, metal-containing compounds, radionuclides, surfactants, and biological residues may

simultaneously occur within the same wastewater stream, generating a chemically competitive environment that can significantly influence contaminant transport, transformation, and removal efficiency [35–38]. A particularly relevant characteristic of hospital wastewater is the presence of numerous substances capable of interacting with treatment materials. Dissolved organic matter (DOM), proteins, amino acids, chelating agents, pharmaceutical metabolites, chloride ions, phosphates, carbonates, and surfactants can compete for adsorption sites and modify surface properties. From an engineering perspective, hospital wastewater is characterized by several features that complicate remediation processes: (i) highly variable pH; (ii) conductivity and ionic strength; (iii) high concentrations of dissolved organic matter; (iv) presence of disinfectants and oxidizing agents; (v) competing cations and anions.

The wastewater generated by nuclear medicine departments constitutes an additional challenge because it contains contaminants with highly diverse chemical speciation and radiological properties. Gadolinium-based contrast agents, radioactive iodine species, technetium complexes, lutetium chelates, and other radiopharmaceutical residues may coexist with conventional hospital pollutants, creating a multicomponent matrix that requires selective monitoring and treatment approaches [39–42].

Another important aspect concerns contaminant concentration levels. Many radiopharmaceutical residues and rare earth elements occur at trace or ultra-trace concentrations, often in the ng L^{-1} to $\mu\text{g L}^{-1}$ range. Consequently, analytical methodologies must combine high sensitivity with speciation capability in order to distinguish between free ions, complexed forms, degradation products, and particulate-associated species.

Conventional municipal wastewater treatment plants are generally not designed to target rare earth elements, gadolinium-based contrast agents, or radiopharmaceutical residues. Biological treatment processes mainly focus on organic matter and nutrient removal and often show limited effectiveness toward highly stable metal complexes and radionuclide-bearing molecules. As a result, several studies have reported the persistence of anthropogenic gadolinium and radiopharmaceutical markers in treated effluents, rivers, groundwater, and even drinking water resources [42,43].

3. Rare Earth Elements and Radiopharmaceuticals in Medical Use

The medical use of REEs and radiometals derives from their chemical–physical properties. The lanthanide series is characterized by a high degree of chemical homogeneity, which originates from the gradual occupation of the inner 4f orbitals while the outer 6s electrons remain available for bonding interactions [44,45]. Since the 4f electrons are effectively shielded by the filled 5s and 5p shells, they have only a limited influence on chemical reactivity. As a result, lanthanides display comparable coordination chemistry, typically adopting the +3 oxidation state, behaving as hard Lewis acids, and preferentially binding to ligands containing oxygen- and nitrogen-donor atoms through predominantly ionic interactions [44–46]. This chemical consistency has made lanthanides particularly valuable in the design of radiopharmaceuticals. Because different radiolanthanides exhibit nearly identical coordination behavior, the same chelating framework can often be used to accommodate multiple radionuclides. Consequently, a single molecular platform can be adapted for either diagnostic imaging or radionuclide therapy simply by replacing one lanthanide with another, thereby streamlining radiopharmaceutical development and production [45–47]. Among the various chelators employed for this purpose, 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) remains the most widely used and clinically established ligand for rare earth elements. DOTA can be readily linked to biological targeting vectors and forms kinetically inert and thermodynamically stable complexes with lanthanide ions. Its effectiveness is demonstrated by the success of radiotherapeutic agents such as ^{177}Lu -

DOTA-TATE and ^{177}Lu -DOTA-TOC, as well as by its application in gadolinium-based magnetic resonance imaging contrast agents [47–52] (see Figure 2).

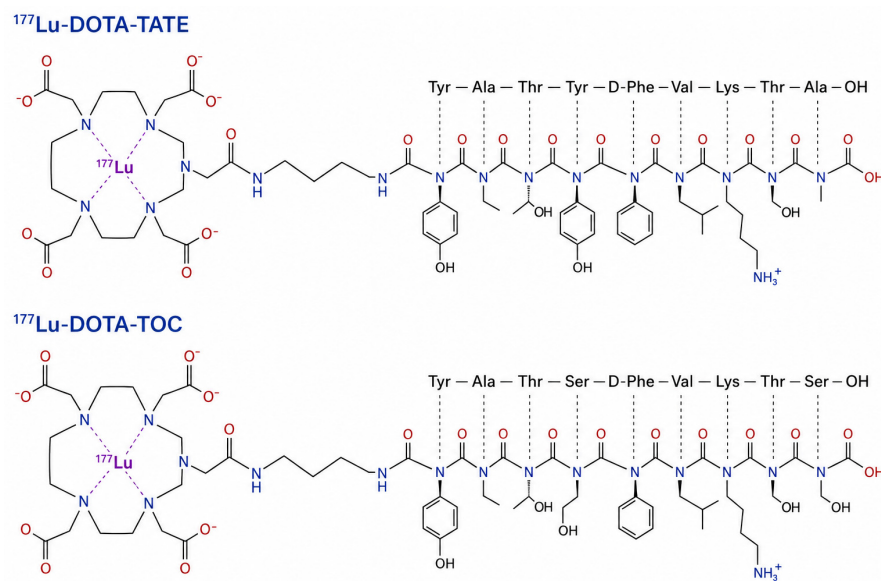


Figure 2. Molecular structures of ^{177}Lu -DOTA-TATE and ^{177}Lu -DOTA-TOC.

In theranostic medicine, a frequent limitation is that diagnostic and therapeutic radionuclides may be associated with different molecular vectors, leading to discrepancies in pharmacokinetics and tissue distribution. The chemical resemblance among lanthanides offers an important advantage in this context. The possibility of incorporating different radionuclides into the same chelator-targeting construct allows the preservation of the molecular architecture while changing only the radioactive metal. This approach promotes greater consistency in biological behavior, increasing the likelihood that diagnostic and therapeutic agents will exhibit similar uptake, retention, and clearance profiles.

Therefore, the use of a common chelator and targeting system for chemically analogous radiolanthanides represents a key strategy for reducing biological variability and improving the correlation between diagnostic imaging and therapeutic outcomes. Such an approach strengthens the foundation of theranostic protocols by enabling a more accurate prediction of treatment performance based on imaging data.

In addition to their analogous coordination chemistry, established synthetic methodologies, and comparable clinical handling, several rare earth radionuclides have attracted increasing attention because of their favorable decay characteristics and their suitability for theranostic applications [47,53]. Interest in these radionuclides stems from their ability to complement currently available diagnostic and therapeutic agents, as well as from the emergence of new isotopes whose clinical implementation has historically been constrained by limited availability and production challenges. Furthermore, some rare earth radionuclides are being investigated as promising alternatives to existing treatments for aggressive or therapy-resistant malignancies, where improved therapeutic efficacy is required. The expanding role of rare earth elements in nuclear medicine is further strengthened by the unique chemical versatility of the lanthanide family, which also includes non-radioactive metals such as gadolinium (Gd^{3+}). In fact, Gd represents a prominent example because it constitutes the paramagnetic center of magnetic resonance imaging (MRI) contrast agents, whereas lutetium, yttrium, gallium, indium, and other radiometals play key roles in diagnostic imaging and targeted radionuclide therapy [7–15].

From an environmental perspective, the occurrence of these contaminants in hospital wastewater cannot be interpreted solely on the basis of their elemental composition. Their

environmental behavior is largely governed by chemical speciation, which determines mobility, persistence, bioavailability, and treatment efficiency.

3.1. Free Gd^{3+} Versus Gadolinium-Based Contrast Agents

Gadolinium is a lanthanide characterized by a high magnetic moment, which makes it particularly suitable for magnetic resonance imaging (MRI). However, free Gd^{3+} ions are highly toxic because of their ability to compete with biologically relevant divalent cations such as Ca^{2+} and Mg^{2+} , interfering with numerous physiological processes. For this reason, gadolinium is never administered clinically as a free ion but is tightly complexed with multidentate organic ligands forming highly stable gadolinium-based contrast agents (GBCAs). The distinction between free Gd^{3+} and GBCAs is fundamental when assessing environmental fate and remediation strategies. Free Gd^{3+} behaves as a typical trivalent lanthanide ion. Depending on pH and water chemistry, it can undergo hydrolysis, form insoluble hydroxides, interact strongly with mineral surfaces, bind to negatively charged adsorbents, and be removed through precipitation or ion-exchange processes.

Consequently, many adsorbent materials, including metal oxides, biochar, graphene derivatives, and AgNP-based composites, exhibit high removal efficiencies when tested against aqueous Gd^{3+} solutions.

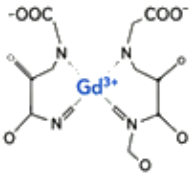
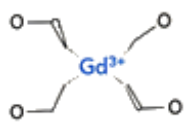
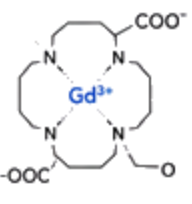
In contrast, clinically relevant GBCAs exhibit completely different physicochemical behavior. In these compounds, gadolinium is encapsulated within macrocyclic or linear chelating ligands specifically designed to prevent metal release. There are two major classes of GBCAs, the linear and macrocyclic GBCAs. Linear GBCA complexes contain open-chain polyaminocarboxylate ligands derived from DTPA (diethylenetriaminepentaacetic acid). Although characterized by high thermodynamic stability, linear complexes generally show lower kinetic inertness than macrocyclic compounds and may undergo partial transmetallation or degradation under specific environmental conditions. The macrocyclic GBCAs possess cage-like macrocyclic structures that encapsulate Gd^{3+} within a rigid molecular cavity. Macrocyclic GBCAs exhibit extremely high thermodynamic stability, very slow dissociation kinetics, exceptional resistance to hydrolysis and limited susceptibility to transmetallation. As a result, they are generally considered the most environmentally persistent gadolinium species.

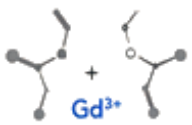
The stability of GBCAs significantly affects their environmental transport. Unlike free Gd^{3+} , these complexes remain predominantly dissolved, exhibit limited adsorption onto sediments, pass through conventional wastewater treatment plants and can be transported over long distances in river systems. Numerous studies have reported elevated dissolved gadolinium concentrations in rivers receiving treated municipal wastewater downstream from hospitals and urban areas. In many cases, the anthropogenic gadolinium can be traced directly to MRI contrast agent consumption.

The distinction between Gd^{3+} and GBCAs is particularly important when evaluating their environmental fate. For free Gd^{3+} removal, adsorption mechanisms are relatively straightforward and may involve electrostatic attraction, surface complexation, ion exchange, and or coordination to oxygen-containing functional groups. However, these mechanisms may be ineffective for intact GBCAs because the metal center is shielded by the chelating ligand. Consequently, remediation strategies must address one of two objectives: direct capture of intact GBCAs (selective molecular recognition, membrane separation, size- and charge-based exclusion, or adsorption of the whole complex) or/and transformation of the chelating ligand (photocatalytic degradation, advanced oxidation processes, or ROS-mediated ligand cleavage). Only after ligand degradation can the released Gd^{3+} become available for adsorption, precipitation, or recovery. This aspect is particularly relevant for plasmonic photocatalytic systems, where reactive oxygen species may contribute to the breakdown of DOTA- or DTPA-based ligands prior to gadolinium

capture. Moreover, the distinction between free Gd^{3+} and intact GBCAs also requires appropriate analytical methodologies. Total gadolinium measurements obtained by ICP-MS do not provide information on speciation and therefore cannot distinguish between free Gd^{3+} , colloidal Gd, intact GBCAs and partially degraded complexes. For environmental monitoring and treatment assessment, speciation-sensitive techniques such as HPLC-ICP-MS, LC-ICP-MS, LC-MS/MS, and capillary electrophoresis-ICP-MS are increasingly required to evaluate the actual performance of remediation technologies (see Table 1). Removal of free Gd^{3+} is useful as a preliminary test of affinity towards lanthanides but should not be used as a direct test of efficacy against clinically relevant GBCAs. For a realistic evaluation, tests should include at least one linear complex, e.g., Gd-DTPA, and one macrocyclic complex, e.g., Gd-DOTA or Gd-BT-DO3A, using speciation methods such as HPLC/IC-ICP-MS. In their critical review, Rogowska et al. highlight gadolinium as an emerging contaminant of aquatic environments, mainly due to the widespread use of gadolinium-based contrast agents in magnetic resonance imaging [53]. Although these compounds are designed as stable chelates to reduce the toxicity of free Gd^{3+} ions in patients, they are largely excreted unmetabolized and pass through conventional wastewater treatment plants with limited removal. As a result, anthropogenic gadolinium has been detected in surface waters, sediments, groundwater, drinking water, and even living organisms, particularly near urban areas and wastewater discharge points. The paper emphasizes that, despite currently low environmental concentrations and limited evidence of acute ecological risk, important knowledge gaps remain regarding long-term toxicity, degradation products, bioaccumulation, environmental fate, and effective removal strategies. Moreover, the work of Brünjes and Hofmann focuses on the occurrence, behavior, and management of anthropogenic gadolinium in freshwater and drinking water systems, mainly originating from the increasing use of gadolinium-based contrast agents in magnetic resonance imaging [12]. The authors emphasize that these compounds are excreted largely unmetabolized, are poorly removed by conventional wastewater treatment plants, and therefore enter rivers, groundwater, and drinking water resources. A key point of the article is that gadolinium-based contrast agents should not be considered completely stable throughout the water cycle, because their degradation depends on ligand structure, environmental conditions, and treatment processes such as UV-based oxidation. The review also discusses the analytical difficulty of distinguishing anthropogenic gadolinium from naturally occurring gadolinium, highlighting the uncertainty caused by different calculation methods for gadolinium anomalies. Finally, the authors propose mitigation strategies, including reverse osmosis, advanced oxidation processes, and especially urine collection from patients after MRI examinations, which could reduce emissions and enable recovery of gadolinium as a technologically critical element.

Table 1. Speciation-sensitive techniques required for environmental monitoring and treatment of free Gd³⁺, colloidal Gd, intact GBCAs and partially degraded complexes.

Gd Species/ GBCA Class	Representative Compounds	Structure	Key Features	Environmental Behaviour	Implications for AgNP- Based Remediation	Analytical Approach (Speciation- Sensitive)	Key Literature (References)
Free Gd ³⁺ (inorganic)	GdCl ₃ , Gd(NO ₃) ₃ , aquo Gd ³⁺	Gd ³⁺ (aq)	• Unchelated lanthanide ion • Strong Lewis acid • Prone to hydrolysis and precipitation	• Adsorbs to surfaces • Forms hydroxides/carbonates • Readily removed by precipitation or ion exchange	• Often high removal by AgNP adsorbents, oxides, graphene, biochar, membranes • Not representative of GBCA removal	• ICP-MS (total Gd) • Speciation needed if free and complexed forms coexist	[53]
Linear ionic GBCAs (negatively charged)	Gd-DTPA (gadopentetate dimeglumine) Gd-EOB-DTPA (gadoxetate disodium)		• Open-chain polyaminocarboxylate ligands • Negatively charged complexes	• Highly soluble and mobile • Less kinetically inert than macrocyclic • Possible degradation/transmetallation	• Adsorption requires capture of whole anionic complex • Ligand degradation or advanced oxidation may be needed	• HILIC-ICP-MS • IC-ICP-MS • LC-ICP-MS • LC-MS/MS (degr. products)	[12]
Linear non-ionic or weakly charged GBCAs	Gd-BOPTA (gadobenate dimeglumine) Other linear DTPA derivatives		• Flexible linear chelate • May contain functional groups affecting protein binding and hydrophilicity	• Mobile in water • Potentially more susceptible to transformation • Can form degradation products	• Removal cannot be inferred from Gd³⁺ adsorption alone • Ligand/surface interactions possible in sensing	• LC-ICP-MS or HILIC-ICP-MS • LC-MS/MS (degr. products)	[12]
Macrocyclic ionic GBCAs (negatively charged)	Gd-DOTA (gadoterate meglumine)		• Cage-like macrocyclic ligand • Highly constrained coordination • Negatively charged complex	• Very high kinetic inertness • Extremely persistent • Passes through WWTPs with little or no removal	• Simple adsorption of Gd³⁺ is poorly representative • Need intact complex capture or ligand degradation	• IC-ICP-MS • HPLC-ICP-MS • LC-ICP-MS • Total ICP-MS alone insufficient	[12]
Macrocyclic non-ionic GBCAs (neutral complexes)	Gd-HPDO3A (gadoteridol) Gd-BT-DO3A (gadobutrol)		• Neutral macrocyclic chelate • Rigid ligand cage around Gd³⁺	• Highly persistent • Weakly particle-reactive • Detected as intact complexes in surface waters	• Membrane separation or selective adsorbents more appropriate • Hybrid AgNP-photocatalysts useful	• IC-ICP-MS • HILIC-ICP-MS • LC-ICP-MS • LC-MS/MS (degr. products)	[12]

Partially degraded GBCAs/transmetallation products	Ligand fragments, mixed-metal complexes, released Gd ³⁺		• Products of photolysis, oxidation, transmetallation or microbial/chemical transformation • Higher reactivity and potentially higher bioavailability • Depends on fragment structure and conditions	• Photocatalysis (e.g., AgNP/TiO₂, AgNP/ZnO) can cleave ligands but must be followed by Gd capture • Integrated workflow: LC-ICP-MS + LC-MS/MS + total ICP-MS	[53]
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3.2. Radiopharmaceuticals

Radiopharmaceutical residues introduce an additional level of complexity because their management depends not only on chemical speciation but also on radionuclide-specific parameters, including half-life, radiation type, activity concentration, and regulatory discharge limits. Short-lived radionuclides may often be managed through decay-storage strategies followed by controlled release, whereas longer-lived or high-activity residues may require selective capture, concentration, or dedicated treatment procedures.

The environmental chemistry of nuclear medicine radionuclides is similarly diverse. Iodine-131 may occur as iodide (I⁻), iodate (IO₃⁻), organoiodine compounds, or volatile iodine species, each exhibiting distinct transport and removal behaviors. Technetium can exist in multiple oxidation states, with pertechnetate (TcO₄⁻) being the dominant and highly mobile form under oxidizing conditions. Likewise, therapeutic and diagnostic radiometals such as ¹⁷⁷Lu, ⁹⁰Y, ⁶⁸Ga, and ¹¹¹In are commonly administered as stable coordination complexes involving DOTA-, DTPA-, NOTA-, or related chelating ligands, which significantly modify their environmental fate compared with their free ionic forms [16–24]. Consequently, hospital sewage systems act as primary collection points for contaminants exhibiting markedly different charges, molecular structures, speciation states, mobilities, and persistence. Studies on hospital effluents and nuclear medicine wastewater have shown that conventional municipal wastewater treatment plants frequently provide incomplete removal of these contaminants, particularly when they are highly soluble, chemically stable, or present at trace concentrations within complex aqueous matrices [25–29]. These observations have important implications for both monitoring and treatment strategies. Analytical methods should ideally provide speciation-sensitive information rather than total elemental concentrations alone. Advanced analytical approaches such as HPLC-ICP-MS, LC-ICP-MS, LC-MS/MS, capillary electrophoresis coupled to ICP-MS, and high-resolution mass spectrometry are increasingly employed to distinguish intact gadolinium chelates, degradation products, free metal species, and radionuclide-bearing complexes. Such information is critical for understanding contaminant transport, persistence, and treatment performance.

Similarly, remediation technologies must operate under realistic wastewater conditions characterized by elevated ionic strength, dissolved organic matter, competing ions, surfactants, disinfectants, pharmaceuticals, and biological metabolites. Materials capable of combining selective recognition, adsorption, catalytic degradation, and sensitive monitoring are therefore particularly attractive [29–34]. Table 2 summarizes the principal classes of rare earth elements and radiopharmaceutical contaminants considered in this review, highlighting their dominant chemical forms, analytical challenges, and potential treatment strategies.

Gwenzi et al. in their review frame high-technology rare earth elements (REEs) as an emerging class of environmental contaminants whose release is increasing with their expanding use in medicine, electronics, renewable energy, petroleum refining, agriculture, livestock production, and industrial processes [62]. China dominates global REE production, with about 98% of total supply reported in the review, while fertilizers,

electronic waste, mining residues, wastewater treatment plants, industrial effluents, and medical facilities represent major anthropogenic sources. Quantitative examples reported in the paper include REE-containing fertilizers with concentrations ranging from 0.38 to 744 mg/kg, REE levels in cereals and vegetables of 74.22 and 94.08 µg/kg, respectively, and a 1.5- to 12-fold increase in gadolinium in Berlin's tap water within three years. Once released, REEs are transported through hydrological and wind-driven processes and partition among soils, sediments, surface water, groundwater, biota, and food chains, with their mobility controlled by pH, redox conditions, dissolved organic matter, mineral phases, and complexing ligands. Ecological effects include phytotoxicity, inhibition of nutrient uptake, oxidative stress, genotoxicity, neurotoxicity, and impacts on soil organisms and aquatic species, whereas human exposure may occur through contaminated food and water, inhalation, occupational contact, and direct medical administration, especially for gadolinium-based contrast agents. Importantly, despite these concerns, REEs and gadolinium are not currently regulated as specific drinking-water parameters in either the European Union or the United States. In the EU Drinking Water Directive, limits exist for selected inorganic or emerging contaminants, such as uranium at 30 µg/L, lead at 10 µg/L, total PFAS at 0.50 µg/L, and sum of PFAS at 0.10 µg/L, but no equivalent parametric value is defined for total REEs or anthropogenic gadolinium. (<https://eur-lex.europa.eu/eli/dir/2020/2184/oj/eng> (accessed on 1 July 2026) "Directive—2020/2184—EN—EUR-Lex) Similarly, the U.S. EPA National Primary Drinking Water Regulations include enforceable standards for contaminants such as uranium at 30 µg/L and radionuclide indicators including alpha particles at 15 pCi/L, beta particles and photon emitters at 4 mrem/year, and combined radium-226/228 at 5 pCi/L, but no maximum contaminant level is established for REEs or gadolinium (<https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations> (accessed on 1 July 2026) "National Primary Drinking Water Regulations|US EPA). Therefore, Gwenzi's review highlights a clear regulatory and scientific gap: although REEs are increasingly detected in environmental and biological matrices, their monitoring, risk assessment, and legal control remain underdeveloped compared with other regulated inorganic contaminants and emerging pollutants.

Moreover, despite the remarkable progress achieved with conventional adsorbents and membrane materials, each class of materials still presents intrinsic limitations when applied to the complex matrix of hospital wastewater. Activated carbon, biochar, zeolites, and other non-Ag adsorbents are widely recognized for their high adsorption capacity toward pharmaceuticals and heavy metals; however, they generally exhibit limited selectivity, poor antimicrobial activity, and are often difficult to regenerate after saturation [65]. Similarly, ion-exchange resins provide excellent removal efficiencies for charged species, including radionuclides and rare earth elements (REEs), but their performance is significantly affected by competing ions and organic matter, requiring frequent chemical regeneration and generating secondary waste streams. Liu et al. in their work provide a valuable contribution to wastewater treatment because they address one of the key limitations in the electrochemical removal of chlorinated organic pollutants: the inefficient use of electrogenerated atomic hydrogen during hydrodechlorination [66]. The authors demonstrate that a Pd-HxWO₃ heterostructured catalyst can significantly enhance the degradation and dechlorination of 2,4-dichlorophenol, a model chlorophenol pollutant frequently associated with contaminated aquatic environments. In particular, the catalyst achieves almost complete 2,4-DCP removal within 1 h and 96% dechlorination after 3 h, outperforming both Pd/GF and HxWO₃/GF electrodes. The relevance for wastewater treatment is strengthened by the broad pH adaptability of the system, its stability over repeated cycles, and its ability to remove other halogenated pollutants such as chloramphenicol, trichlorophenol and triclosan. Importantly, the paper shows that

hydrogen spillover from HxWO_3 to Pd improves the generation, transfer and utilization of reactive H^* , thereby increasing Faradaic efficiency and reducing the kinetic mismatch typical of conventional Pd-based systems. These results suggest that hydrogen-spillover-assisted electrocatalysis could be a promising strategy for treating real wastewater streams containing persistent chlorinated contaminants, but further studies on complex matrices, long-term operation and energy consumption would be necessary before practical implementation. Metal-organic frameworks (MOFs) have emerged as highly attractive alternatives because of their exceptionally high surface area, tunable pore architecture, and chemically tailorable adsorption sites, enabling outstanding removal efficiencies for a broad range of contaminants [67]. Nevertheless, many MOFs still suffer from limited hydrolytic stability, relatively high synthesis costs, and concerns regarding long-term durability under realistic wastewater conditions, despite considerable advances in defect engineering and composite design. Conventional polymeric or ceramic membranes efficiently separate suspended solids and microorganisms but are inherently susceptible to membrane fouling and biofilm formation, often requiring additional functionalization to impart catalytic or antimicrobial properties. In contrast, AgNP-based hybrid nanomaterials integrate several complementary functions within a single platform. In addition to exhibiting broad-spectrum antimicrobial activity, silver nanoparticles can catalyze the degradation of organic pollutants, provide plasmonic sensing capabilities, enhance adsorption through synergistic interactions with engineered supports or functional ligands, and simultaneously mitigate membrane biofouling. When immobilized onto polymers, porous supports, or inorganic matrices, AgNPs also display improved colloidal stability, reduced silver leaching, and enhanced recyclability, overcoming many of the environmental concerns associated with free nanoparticles. Consequently, Ag-based hybrid systems represent a multifunctional strategy capable of combining adsorption, catalysis, sensing, and membrane protection in a single material, reducing process complexity while improving treatment efficiency and facilitating material recovery and circular reuse.

Table 2. Principal classes of rare earth elements and radiopharmaceutical contaminants occurring in hospital wastewater.

Contaminant Class	Main Sources	Predominant Chemical Forms	Analytical and Treatment Challenges	Potential Treatment Strategies	Ref.
Anthropogenic gadolinium (Gd)	MRI examinations and patient excretion	Gd-DOTA, Gd-DTPA, Gd-HPDO3A and other GBCAs	High thermodynamic stability of Gd-chelates, persistence in aquatic environments, and poor removal by conventional WWTPs	Functionalized adsorbents, membrane filtration, advanced oxidation processes (AOPs), selective chelating materials	[54,55]
Diagnostic radiometals	Nuclear medicine imaging procedures	$^{99\text{m}}\text{Tc}$ complexes, ^{68}Ga -labeled tracers, ^{111}In compounds	Short half-lives, ultra-trace concentrations, radionuclide speciation, and radioprotection constraints	Decay storage, ion exchange, selective adsorption, engineered nanocomposites	[56]
Therapeutic radiometals	Targeted radionuclide therapy	^{177}Lu -DOTA-TATE, ^{177}Lu -DOTA-TOC, ^{90}Y -labeled compounds, ^{223}Ra salts	Radioactive waste management, discharge limits, and complex aqueous matrices	Selective sorbents, ligand-functionalized adsorbents, magnetic nanocomposites	[53,57]
Radioiodine species	Thyroid cancer diagnosis and therapy	I^- , IO_3^- , and ^{131}I -containing waste streams	High mobility in water systems and need for	Ag-zeolites, Ag-supported materials, AgI precipitation, ion-exchange systems	[58–60]

			decay or capture before discharge		
Lanthanide residues from medical and research activities	Research laboratories, pharmaceutical production, hospital facilities	La ³⁺ , Ce ³⁺ /Ce ⁴⁺ , Nd ³⁺ , Eu ³⁺ and mixed REE species	Similar chemical behavior among REEs, low concentrations, and matrix interferences	Chelating adsorbents, biosorbents, membrane technologies, hybrid nanomaterials	[61–63]
Mixed hospital wastewater contaminants	Combined hospital effluents	REE complexes, radiopharmaceutical residues, pharmaceuticals, organic matter, salts, and phosphates	Competition for adsorption sites, dissolved organic carbon effects, and colloidal instability	Multifunctional nanomaterials, AgNP-based composites, integrated membrane-biological systems	[64]

4. Engineering AgNP-Based Hybrid Nanomaterials for Hospital Wastewater Treatments

AgNPs are commonly defined as silver particles with at least one dimension below 100 nm, although their behavior is controlled less by size alone than by the combination of size distribution, shape, crystallinity, oxidation state, surface charge, ligand shell, and surrounding matrix. At the nanoscale, silver exposes a large fraction of surface atoms, which increases catalytic and interfacial reactivity. Its localized surface plasmon resonance (LSPR) produces intense optical responses that are useful in colorimetric assays, surface-enhanced Raman spectroscopy (SERS), plasmon-assisted photocatalysis, and nanosensor architectures [26–34]. The importance of structural order and interfacial design has been shown in photonic and self-assembled polymeric nanosphere systems, where nanoscale organization strongly affects optical response [68,69]. Similar principles apply to noble metal nanoparticles: ligand-bridged architectures, fluorescently labeled AgNPs, and dye-functionalized nanosystems illustrate how organic shells, coordination motifs, and chromophore coupling can tune plasmonic and fluorescence properties [70,71]. These lessons are directly relevant to wastewater monitoring, where the signal generated by a nanosensor depends on surface accessibility, hotspot formation, colloidal robustness, and the ability to discriminate target species from a complex background. Surface engineering also provides a bridge between fundamental nanochemistry and practical water treatment. Studies on functional polymeric nanoparticles, mixed-thiol-protected gold nanoparticles, hydrophilic AgNPs incorporated into niosomes, and bioactive-molecule-functionalized noble metal nanoparticles show that charge, capping chemistry, hydrophilicity, ligand packing, and organic coatings can regulate colloidal behavior and biological response [72–75]. For wastewater applications, these parameters are not secondary details; they determine whether AgNPs aggregate, dissolve, bind to natural organic matter, release Ag⁺, or remain attached to a recoverable support. AgNPs are most often prepared by chemical reduction of silver salts such as AgNO₃ using reductants including borohydride, citrate, ascorbate, hydrazine, or plant-derived polyphenols. Stabilizers such as citrate, thiols, polymers, or polyvinylpyrrolidone are typically introduced to limit uncontrolled growth and aggregation. Greener synthesis methods have gained increasing attention because they can reduce the use of hazardous reagents and introduce biogenic capping layers that may improve compatibility with environmental applications [32,34,76,77]. Plant extracts, microorganisms, polysaccharides, proteins, and agricultural residues can act simultaneously as reducing and stabilizing agents, although batch-to-batch reproducibility and surface composition must be carefully verified. Hybridization with semiconductors and photoactive supports is another major design route. Work on ZnO-sensitized systems, Pt nanoparticles on electrospun TiO₂ nanofibers, and photoelectrochemical NiO-based cathodes highlights

the broader relevance of metal/oxide interfaces, nanostructured semiconductors, and surface sensitization in catalytic and photoactive devices [78–80]. In Ag-based photocatalysts, AgNPs can act as plasmonic sensitizers, electron sinks, or interfacial charge mediators. These roles reduce electron–hole recombination and favor reactive oxygen species generation, which is useful for degrading pharmaceuticals, dyes, disinfectants, and other organic micropollutants that coexist with REEs and radionuclides.

Immobilization is essential for moving from laboratory suspensions to safer treatment technologies. AgNPs have been immobilized on activated carbon, graphene oxide, biochar, zeolites, magnetic nanoparticles, silica, chitosan, hydrogels, and other polymeric matrices [81–90]. Activated carbon and biochar contribute high surface area and adsorption sites, while AgNPs add antimicrobial and catalytic activity [81,83]. Graphene oxide improves electron transfer and provides a two-dimensional scaffold [82]. Zeolitic Ag systems are especially relevant for iodine capture because aluminosilicate frameworks provide ion-exchange pathways and silver can immobilize iodide through AgI formation [84]. Magnetic supports simplify post-treatment recovery, whereas silica, chitosan, and hydrogel matrices improve mechanical stability, wettability, and ligand accessibility [85–90]. Structured devices such as three-dimensional printed AgNP-containing hydrogel filters further illustrate the shift from dispersed nanoparticles toward engineered, retrievable architectures [89]. Membrane incorporation is particularly attractive for hospital wastewater because microbial fouling is a major operational limitation. AgNP-modified membranes can increase hydrophilicity, inhibit bacterial colonization, improve flux stability, and provide an antimicrobial barrier in ultrafiltration, nanofiltration, and membrane bioreactor configurations [91–93]. In parallel, Ag/TiO₂, Ag/ZnO, and related plasmonic nanohybrids can expand visible-light activity and enhance oxidative transformation of persistent organics through improved charge separation and reactive oxygen species production [34,94–97]. The most promising systems are therefore not bare AgNP suspensions but supported and multifunctional platforms that integrate antimicrobial protection, photocatalysis, adsorption, and controlled recovery.

Figure 3 shows a scheme of the surface and support engineering strategies employed for AgNP-based hybrid nanomaterials.

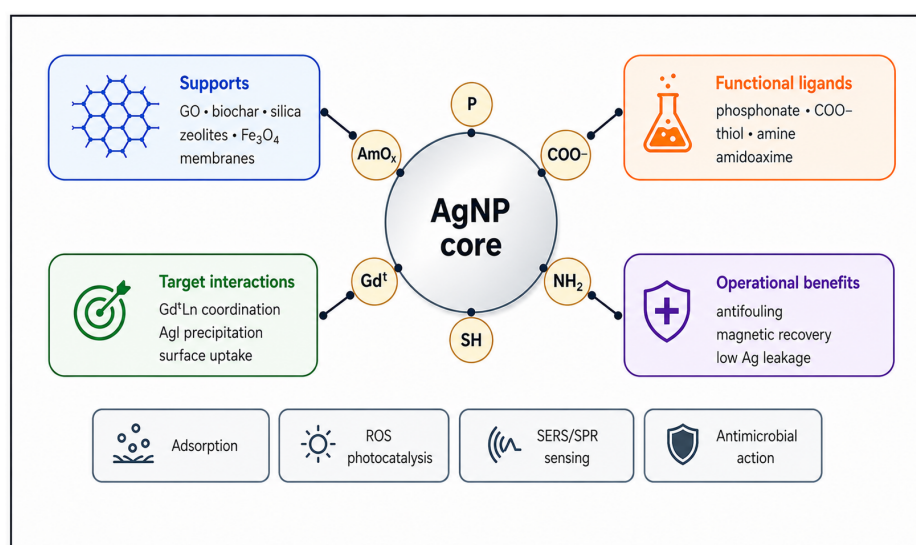


Figure 3. Schematic illustration of AgNP-based hybrid nanomaterials. The combination of functional ligands (e.g., phosphonate, carboxylate, thiol, amine, and amidoxime groups) and immobilization matrices (e.g., graphene oxide, biochar, silica, zeolites, Fe₃O₄, and membranes)

modulates target interactions, stability, recovery, and silver release, ultimately enhancing adsorption, photocatalytic activity, SERS/SPR sensing performance, and antimicrobial efficacy.

The physicochemical properties and performance of AgNPs can be tailored through the rational selection of surface functional ligands (e.g., phosphonate, carboxylate, thiol, amine, and amidoxime groups) and immobilization supports (e.g., graphene oxide, biochar, silica, zeolites, Fe_3O_4 , and polymeric membranes). These modifications regulate nanoparticle stability, surface reactivity, target-specific interactions, and silver ion release while improving resistance to aggregation and facilitating material recovery.

Table 3 highlights substantial differences between Ag-based hybrid platforms, although the reported metrics reflect distinct target processes. For membrane applications, the GO-AgNP-coated cellulose acetate membrane developed by Sun et al. reduced the relative decline in permeate flux after 24 h from 88% for the unmodified membrane to 46%, while achieving 86% inactivation of *Escherichia coli* after 2 h, demonstrating the combined antifouling and antibacterial benefits of graphene-supported AgNPs [82]. Magnetic platforms offer a different advantage: Najafpoor et al. reported mean particle sizes of 41 nm for Fe_3O_4 nanoparticles and 34 nm for Ag-loaded magnetic nanoparticles, with saturation magnetizations of 62 and 67 emu g^{-1} , respectively [85]. Under optimized conditions (105 mg L^{-1} of nanomaterial, 70 min of contact time, and 55% wastewater contamination), the systems produced mean log reductions of 0.65, 0.48, and 0.58 for total coliforms, fecal coliforms, and heterotrophic bacteria, along with 30.40% COD removal; Ag loading provided an additional microbial reduction of approximately 0.06 log and a 6.16 percentage point improvement in COD removal compared to unmodified magnetic nanoparticles. The biochar/ Fe_3O_4 -Ag catalyst reported by Taheri et al. maintained catalytic activity for at least ten consecutive cycles and could be recovered magnetically, although this study evaluated the reduction reactions of nitroaromatics, aldehydes, and ketones rather than hospital wastewater contaminants [83]. Therefore, it supports the recoverability of the platform but not its direct efficacy against rare earths or radiopharmaceuticals. For Ag-zeolite composites, Gicheva et al. found minimum inhibitory concentrations against *E. coli* of 0.8 mg mL^{-1} for the heat-treated Ag zeolite and 1.0 mg mL^{-1} for the citrate-reduced material, while reduction with NaBH_4 generated larger and more aggregated AgNPs up to 55 nm and lower antibacterial activity [84]. Finally, the $\text{Ag}_2\text{O}/\text{MoO}_3/\text{SiO}_2$ photocatalyst reported by Rajhi et al. contained an optimized Ag_2O loading of 8 wt%, a surface area of 151.59 $\text{m}^2 \text{g}^{-1}$, and a band gap of 2.39 eV. At a concentration of 2.0 g L^{-1} , complete photoreduction of Hg(II) was achieved within 30 min, with a rate of 60.43 $\mu\text{M min}^{-1}$ and 95% activity retention after five cycles [86]. Depending on the chosen surface chemistry and support matrix, AgNP-based hybrids can be engineered for enhanced adsorption, ROS-mediated photocatalysis, SERS/SPR sensing, and antimicrobial applications, providing multifunctional platforms with improved efficiency, selectivity, and reusability in environmental and biomedical fields.

Table 3. Silver nanoparticle (AgNP)-based platforms useful for hospital wastewater treatment, with particular attention to design advantages and limitations.

AgNP Platform	Primary Role of Support or Ligand	Dominant Mechanism	Advantages for Hospital Wastewater	Main Limitation or Control Point	Ref.
AgNP/activated carbon or AgNP/biochar	High surface area, porosity, organic affinity	Adsorption plus antimicrobial action	Suitable for polishing mixed organic and metal-containing streams	Requires regeneration and control of Ag leaching	[83]

AgNP/graphene oxide	Conductive, oxygen-rich and high-area 2D support	Electron transfer, adsorption, SERS enhancement	Useful for sensing and catalytic hybrid materials	Aggregation and cost must be managed	[82,98]
Silica-supported AgNPs	Chemically robust porous matrix	Nanoparticle stabilization and surface adsorption	Good dispersion and lower particle detachment	Needs additional ligands for REE selectivity	[84]
Ag-zeolites	Ion-exchange aluminosilicate framework	Iodide capture as AgI and ion exchange	Relevant for radioiodine-containing streams	Performance depends on competing ions and regeneration strategy	[99]
Fe ₃ O ₄ /Ag composites	Magnetic recovery and solid-liquid separation	Adsorption, antimicrobial action and recoverability	Minimizes release of free nanoparticles after treatment	Magnetic core oxidation and coating stability must be checked	[85,87]
AgNP-polymeric membranes	Hydrophilic/antifouling membrane interface	Size exclusion, antimicrobial action and anti-biofouling	Compatible with MBR, UF and NF configurations	Long-term silver release and permeability decline require testing	[91–93]

4.1. Treatment of Hospital Wastewater Containing REEs and Radiopharmaceutical Residues

The treatment of hospital wastewater containing REEs and radiopharmaceutical residues requires materials able to operate in a chemically crowded matrix. Dissolved organic matter, carbonate, phosphate, chloride, sulfate, calcium, magnesium, disinfectants, antibiotics, and chelating ligands such as EDTA, DTPA, and DOTA can all compete for active sites or change the speciation of target contaminants [1–6]. Bare AgNPs may provide antimicrobial or catalytic benefits, but they are usually not sufficiently selective for stable GBCA molecules or radiometal–chelate complexes. For this reason, the performance of AgNP-based materials depends strongly on surface functionalization and support selection. Ligand design is central to selective uptake. Phosphonate, carboxylate, amine, thiol, amidoxime, catechol, and EDTA-like groups can be introduced on AgNPs or on AgNP-containing supports to increase affinity for lanthanides and radionuclides. Functionalized graphene adsorbents for Gd, silver-functionalized materials for radionuclide capture, AgNP-containing membranes for radioactive wastewater, and nanoadsorbents for selective lanthanide separation all indicate that the density, accessibility, and chemical identity of binding sites are more important than silver content alone [99–102]. Phosphonate- and carboxylate-rich surfaces are particularly relevant for hard trivalent cations such as Gd³⁺ and Lu³⁺, whereas sulfur- and nitrogen-containing ligands can contribute to softer metal binding, colloidal stabilization, and interfacial selectivity. AgNP-based platforms may also assist in detection. LSPR, SERS hotspots, and interfacial electron transfer provide signal-amplification mechanisms for trace monitoring of metal-containing contaminants and radionuclide proxies [27–29,33]. Bifunctionalized AgNPs used for Fe(III) detection demonstrate how capping chemistry can simultaneously control sensitivity, selectivity, and safer environmental behavior [102]. Fluorescent polymeric nano- and microplastic tracers further show how labeled particulate systems can support bioimaging and fate assessment in ecotoxicological studies, providing tools

that may be adapted to track engineered nanomaterials in wastewater and receiving waters [103]. For radiopharmaceutical residues, treatment strategies must be selected according to radionuclide chemistry. Silver-containing zeolites and related supports are attractive for iodine because iodide can be trapped through adsorption and AgI formation [19,84]. Technetium species may require redox-sensitive materials or hybrid adsorbents able to bind reduced or oxidized forms. Radiometals such as ^{177}Lu , ^{90}Y , ^{68}Ga , and ^{111}In are better approached with chelating groups and oxide or polymer supports that mimic lanthanide/radiometal coordination environments [24,98–101]. AgNPs should therefore be considered as one functional component within a larger material architecture, rather than as a universal adsorbent for all radiopharmaceutical residues. An integrated treatment train could combine source segregation and decay storage for radioactive streams, followed by advanced polishing units based on immobilized AgNP platforms. A realistic sequence may include equalization, membrane filtration with anti-biofouling AgNP-containing membranes, photocatalytic oxidation for organic micropollutants and chelating ligands, and a final adsorption or ion-exchange step using functionalized supports for REEs and radiometals. Such a configuration would use the antimicrobial properties of AgNPs where biofouling is most relevant, while relying on tailored ligands and recoverable supports for selective contaminant capture.

4.2. Safe-by-Design AgNP Platforms

From an application perspective, the key challenge is not simply to synthesize highly active AgNPs but to build treatment units that remain efficient, recoverable, and environmentally acceptable under continuous operation. Hospital wastewater varies during the day according to clinical activity, cleaning procedures, patient load, and the scheduling of radiology or nuclear medicine treatments. AgNP-based systems should therefore be evaluated under dynamic conditions rather than only in single-solute batch tests. Parameters such as contact time, hydraulic residence time, fouling rate, backwashing tolerance, regeneration efficiency, and performance after repeated cycles are essential for assessing technological relevance.

A safe-by-design AgNP platform should satisfy at least four criteria. First, silver must be immobilized strongly enough to limit nanoparticle detachment and uncontrolled Ag⁺ release. Second, the support should provide a function that silver alone cannot deliver, such as magnetic recovery, membrane separation, ion exchange, ligand-assisted lanthanide binding, or photocatalytic activity. Third, the material should remain active in the presence of competing ions and natural organic matter. Fourth, end-of-life management must be considered from the beginning, including regeneration, concentration of captured radionuclides, and disposal or recycling of spent adsorbents. These requirements are consistent with evidence that the toxicity and fate of nanosilver are influenced by dissolution, capping, aggregation, and interactions with biological interfaces [103–110].

For REE-containing wastewater, adsorption data should be interpreted with caution. Many studies report high uptake capacities using free metal ions in simplified water, but hospital effluents often contain Gd, Lu, Y, Ga, or In as stable chelated species. A material that efficiently captures Gd³⁺ may perform poorly toward Gd-DTPA or Gd-DOTA unless the surface promotes ligand exchange, electrostatic association, or adsorption of the intact complex. Therefore, future experiments should compare free ions, clinically relevant contrast agents, and spiked real wastewater. They should also report speciation-sensitive measurements, when possible, because total metal removal alone does not reveal whether the contaminant was degraded, adsorbed as an intact complex, or transformed into a different species.

For radiopharmaceutical residues, process design must integrate radioprotection. AgNP-based adsorbents can be useful only after activities, half-lives, and discharge rules have been considered. Short-lived radionuclides may be better managed through decay tanks before polishing, while longer-lived or particle-reactive species may justify selective concentration. When adsorbents are used, the spent material becomes a secondary waste stream and must be handled according to radioactive-waste procedures. This issue favors compact, high-capacity, magnetically recoverable, or cartridge-type AgNP systems that minimize the volume of radioactive solid waste.

Finally, performance evaluation should include ecotoxicological endpoints, not only removal percentages. A treatment material that removes a target pollutant but releases bioavailable silver may shift the environmental burden rather than reduce it. For this reason, leaching tests, Ag speciation, antimicrobial impact on beneficial sludge microorganisms, phytotoxicity assays, and aquatic organism tests should accompany chemical analyses. The most convincing future platforms will be those that demonstrate contaminant removal, low silver release, retained activity after regeneration, and reduced biological impact in parallel (Figure 4). Large-scale implementation of AgNP technologies still faces challenges related to synthesis costs, silver consumption, long-term stability, and regulatory approval.



Figure 4. Conceptual framework for the safe-by-design development of silver nanoparticle (AgNP)-based platforms for the treatment of rare earth element (REE)-containing wastewater and radiopharmaceutical residues. The scheme highlights the four key design principles: (i) stable immobilization of AgNPs to minimize silver release; (ii) integration of support-specific functionalities (e.g., magnetic recovery, membrane separation, ion exchange, ligand-assisted binding, or photocatalysis); (iii) robust performance under complex wastewater conditions; (iv) end-of-life management through regeneration, selective concentration of contaminants, and safe disposal or recycling. The workflow also emphasizes the importance of evaluating ecotoxicological endpoints, including silver leaching, biological impact, regeneration efficiency, and environmental safety, alongside contaminant removal performance.

4.3. Analytical Validation and Benchmarking Requirements

For publication-quality evidence, AgNP-based treatment materials should be benchmarked using analytical workflows that distinguish removal, transformation, and

mere signal suppression. In the case of GBCAs, total Gd measurements by ICP-MS are useful for mass balance, but they do not identify whether the original contrast agent remains intact, is partially decomplexed, or has been captured through adsorption of the whole chelate. Coupling chromatographic separation with element-specific detection, when available, can clarify speciation and provide stronger mechanistic information. Similar considerations apply to radiopharmaceutical residues; gamma spectrometry, liquid scintillation counting, or radiochemical separation should be selected according to radionuclide emission, half-life, and expected chemical form [7–24].

Benchmarking should also include controls that are often missing in early-stage nanomaterial studies. A supported AgNP system should be compared with the bare support, unsupported AgNPs, a non-silver analog, and a conventional adsorbent or membrane under identical conditions. This comparison helps to separate the contribution of silver from the role of surface area, porosity, ligand chemistry, and membrane structure. In adsorption tests, pH, ionic strength, dissolved organic carbon, chloride, sulfide, phosphate, carbonate, calcium, and magnesium should be reported because they influence both contaminant speciation and AgNP stability. For membranes, flux recovery ratio, irreversible fouling, bacterial adhesion, Ag leaching, and performance after cleaning cycles are as important as initial contaminant rejection [91–93,111,112].

Kinetic and regeneration data are equally important. High equilibrium uptake in a 24 h batch test does not necessarily translate into a useful continuous process. Hospital wastewater polishing units require rapid mass transfer, predictable breakthrough curves, and regeneration protocols that do not generate larger secondary waste streams than the original problem. For radionuclide-containing matrices, regeneration must be evaluated carefully because desorption solutions may become concentrated radioactive liquids. Therefore, cartridge replacement, solidification of spent media, or decay storage of compact adsorbents may be more realistic than repeated chemical regeneration in some clinical contexts [16–24,98–101].

Finally, treatment performance should be reported together with residual toxicity and silver release. A complete dataset should include target removal, total Ag and dissolved Ag, particle detachment from supports, antimicrobial effect before and after use, and ecotoxicological response of treated effluent. Such integrated benchmarking would allow comparison among Ag-zeolites, Ag-carbon materials, Ag-polymer membranes, magnetic Ag composites, and Ag-doped hydrogels on the basis of both efficacy and environmental safety [81–113].

A further point concerns reporting harmonization. Studies should specify whether removal is calculated from dissolved, particulate, or total concentrations and whether samples were filtered before analysis. This is especially important for AgNP-containing systems because particles, dissolved Ag, adsorbed target species, and matrix-derived colloids may coexist in the same sample. Without a clear separation protocol, apparent removal may reflect retention on filters, precipitation, or analytical artefacts rather than genuine uptake by the designed material. Reporting particle size distribution, zeta potential, surface ligand density, Ag loading, leaching after treatment, and mass balance for both the target contaminant and silver would make comparison among materials more reliable [26–34,81–93,111,112].

Technology readiness should also be assessed at the level of the treatment module rather than only at the level of the nanomaterial. A promising AgNP composite must be manufactured reproducibly, packed or immobilized without loss of activity, operated with realistic flow rates, and monitored without requiring excessive sample preparation. For hospital implementation, compact cartridges, membrane cassettes, magnetic separators, or 3D-printed filters may be more realistic than free nanoparticle dosing. These formats can be placed downstream of decay tanks or equalization units and removed as

controlled solid wastes when exhausted. Such engineering choices are essential for reconciling remediation efficiency with occupational safety, regulatory traceability, and avoidance of secondary nanoparticle pollution (see Table 4) [89–93,111,112,114–119].

Most AgNP-based systems have been evaluated using simplified aqueous solutions or model contaminants, whereas hospital effluents represent chemically complex matrices containing dissolved organic matter, competing ions, pharmaceuticals, disinfectants, and stable metal–chelate complexes. Therefore, performance should be assessed using both synthetic solutions and real hospital wastewater spiked with clinically relevant compounds, including Gd-DOTA, Gd-DTPA, ^{177}Lu -DOTATATE, and representative technetium-99m radiopharmaceuticals. Particular attention should be paid to chemical speciation, since removal efficiencies determined for free Gd^{3+} or Lu^{3+} ions cannot be considered representative of intact coordination complexes. Consequently, adsorption experiments should be complemented by speciation-sensitive analytical techniques, such as LC-ICP-MS or HPLC-ICP-MS, capable of distinguishing free ions, intact chelates, and degradation products before and after treatment.

Table 4. Key experimental validation steps recommended for the development and environmental assessment of silver-based treatment systems targeting gadolinium-based contrast agents (GBCAs) and radionuclides in hospital wastewater. The framework integrates performance evaluation with sustainability and regulatory considerations, including realistic matrices, speciation, adsorption kinetics, selectivity, material stability, ecotoxicity, and waste management.

Validation Level	Recommended Experiment	Key Output	Reason for Inclusion
Matrix realism	Test in synthetic wastewater, hospital effluent and post-biological effluent	Removal under increasing complexity	Distinguishes intrinsic activity from matrix-tolerant performance
Speciation control	Combine total element analysis with speciation-aware methods where possible	Free, complexed, particulate and adsorbed fractions	Prevents overestimation of GBCA or radiometal removal
Kinetics and flow	Batch kinetics plus column or membrane-flow tests	Rate constants, breakthrough curves and flux data	Supports translation from beaker tests to treatment modules
Selectivity	Evaluate competition from Ca, Mg, Fe, phosphate, carbonate, chloride and DOC	Selectivity coefficients or retained capacity	Hospital wastewater contains strong inorganic and organic interferents
Silver release	Measure total Ag, dissolved Ag and particle detachment before and after use	Secondary pollution indicators	Confirms that remediation does not introduce a new contaminant
Regeneration	Perform multiple adsorption/desorption or filtration cycles	Capacity retention and structural stability	Determines feasibility and waste generation
Residual toxicity	Include microbial, algal, plant or invertebrate bioassays	Ecotoxicological profile of treated water	Links chemical removal to environmental safety

End-of-life handling	Assess spent adsorbent, radioactive concentrate and Ag-bearing sludge	Waste class and disposal route	Necessary for radioprotection and regulatory compliance
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Material characterization should also include adsorption kinetics, equilibrium isotherms, selectivity under competitive conditions, regeneration efficiency, and long-term structural stability. Recent studies have demonstrated that AgNP-based materials can be successfully integrated into advanced filtration platforms, including 3D-printed PEGDA hydrogels for heavy metal removal, which combine tailored architecture with facile recovery and mechanical robustness, providing a promising strategy for future multifunctional treatment devices [90]. Similarly, chitosan-supported AgNP composites have shown effective antimicrobial activity and wastewater disinfection, highlighting the dual role of silver as both a catalytic and biocidal component [91]. These findings indicate that future systems should simultaneously evaluate contaminant removal, bacterial inactivation, and operational durability.

For membrane-based technologies, antifouling behavior represents an equally important validation parameter. Recent reviews emphasize that embedding AgNPs into polymeric membranes significantly reduces microbial colonization and biofilm formation, thereby extending membrane lifetime and improving process stability [92,94,111]. The incorporation of AgNPs into cellulose acetate/chitosan mixed-matrix membranes or Ti₃C₂T_x-PLA composite membranes has further demonstrated enhanced hydrophilicity, permeability, antibacterial performance, and resistance to fouling under realistic wastewater conditions [93,112].

5. Conclusions and Perspectives

AgNP-based hybrid nanomaterials offer a versatile toolbox for the monitoring and treatment of hospital wastewater containing REEs and radiopharmaceutical residues. Their value derives from the combination of plasmonic sensing, antimicrobial action, catalytic activity, membrane anti-biofouling, adsorption, and compatibility with engineered supports. Nevertheless, the evidence reviewed here indicates that bare AgNPs are not sufficient for selective removal of stable GBCAs or radiometal–chelate complexes. Functionalized, immobilized, and recoverable materials are required to translate nanosilver chemistry into practical treatment systems. Future research should move beyond proof-of-concept experiments and address real hospital wastewater, clinically relevant contrast agents, radiopharmaceutical speciation, regeneration, silver release, and ecotoxicity. Smart multifunctional platforms may combine online sensing, selective adsorption, photocatalytic oxidation, radionuclide recovery, monitoring, and sustainable nanofabrication. If designed according to safe-by-design principles, AgNP-based systems could become part of modular treatment trains that reduce microbial load, mitigate persistent organic contaminants, and improve control of metal-containing and radioactive residues released by modern medical practice. Overall, the key message is that AgNP-based technologies should not be viewed as stand-alone solutions, but as integrated, engineered, and safety-validated components of advanced wastewater treatment strategies for healthcare-derived contaminants.

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