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Review

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A Review of Nanoparticles Utilized in the Removal of Radioactive Iodine from Wastewater Streams

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ABSTRACT

Iodine contributes a major chunk of radioactive waste due to its broad spectrum of unstable isotopes. The environmental dissemination of these isotopes stems from nuclear reactors, the nuclear medicine industry, and nuclear calamities. Owing to the harmful effects of radioiodine on human health, many materials have been tested to remove iodine from wastewater streams. Among these materials, nanoparticles have shown significant ability because of their nanosized effects, high specific surface area, and ability to carry multiple functional groups. This paper, therefore, aims to review the nanoparticles that have shown sufficient adsorption for iodine in aqueous media. The manuscript seeks to elucidate the rationale for selecting specific nanomaterials and expound upon the underlying mechanisms governing the adsorption rate. It also discusses the necessary conditions for optimizing adsorption rates and the inherent limitations of these nanomaterials.

Key Words: Radioiodine, Nanoparticles, Adsorption capacity, Mechanism of adsorption

Introduction

Management of radioactive waste material is the most pressing issue in the present world. Nuclear materials serve indispensable roles in diverse domains from fulfilling our energy needs to advancing medical treatments. Despite their significance, the current radioactive waste handling is inadequate to safeguard humanity. Notably, the key radioiodine contaminants are ^{131}I ($t_{1/2}$ = 8 d), ^{129}I ($t_{1/2}$ = 1.57 × 107 y), ^{125}I ($t_{1/2}$ = 59 d), and ^{123}I ($t_{1/2}$ = 13.2 h) (1). Among these, ^{131}I and ^{129}I are fission products of uranium and plutonium, and nuclear reactor facilities release them into water streams in small amounts due to inadequate filtration methods (2). Moreover, the Chornobyl and Fukushima disasters released substantial radioactivity into wastewater streams due to precipitation, fall-outs, and after-accident discharges (3). ^{123}I and ^{125}I are produced artificially for imaging, biological assays, and therapies in the nuclear medicine industry. So, the cancer patients undergoing treatment mix them with water through their body secretions (4).

Iodine is known for its adverse effects on human

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health such as metabolic imbalances, genetic mutations, thyroid cancer, leukemia, and mental disorders (5). Additionally, iodine released into water reaches seas where it accumulates in seaweeds and becomes part of the food chain imparting its pernicious effects to many species (6). These detrimental effects have necessitated research to remove radioactive iodine from wastewater streams. In this regard, researchers have investigated a broad spectrum of materials. Still, none have shown the necessary resilience for commercial applications, owing to their slow dynamics, high cost, or difficult regeneration procedures (7). Carbon-based materials impregnated with TEDA and silver-exchanged zeolites were investigated with the inception of the nuclear industry in the 1960s with a special focus on nuclear accidents. However, interest in the field rose dramatically after the Fukushima disaster leading to the testing of many new materials to contain radioactive iodine (8). This time new sorbents such as mesoporous silica (9, 10), silver functionalized silica (11, 12), titanosilicates (13), silver-impregnated alumina (14), silver-impregnated aerogels (15), ion exchange resins, organic polymers, and covalent organic frameworks were scrutinized (8). However, in the present paper, we essentially focus on the nanomaterials used to remove radioiodine from water (Figure 1). Modern nanomaterials have significant potential to advance next-generation decontamination materials on the grounds of their large surface area, higher adsorption capacity, and greater chemical affinity for radioisotopes. Additionally, adsorption sites on nanomaterials can be easily functionalized to remove multiple radioisotopes (16). Subsequent sections discuss the research in immobilizing radioiodine from water using carbon-based, magnetic, titanium-based, and metal-doped nanomaterials (Figure 2).

Carbon-based Nanomaterials

Carbon has been among the foremost materials employed in the initial stages of radioactive decontamination. Carbon both in its pristine and modified forms shows removal efficiency for different radioactive contaminants. Carbon nanotubes (CNTs), featuring cylindrical nanostructures, have diameters less than a nanometer. They are made of carbon atoms arranged in a unique hexagonal lattice pattern. The cylindrical

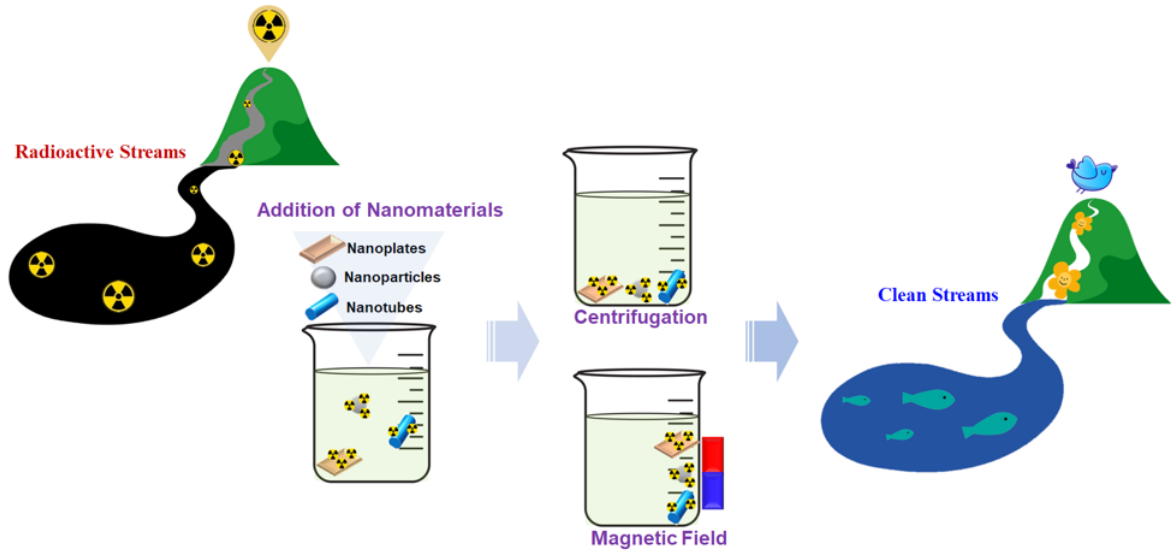

Figure 1. Schematic overview of nanomaterials utilized in the removal of radioactive iodine from wastewater streams.

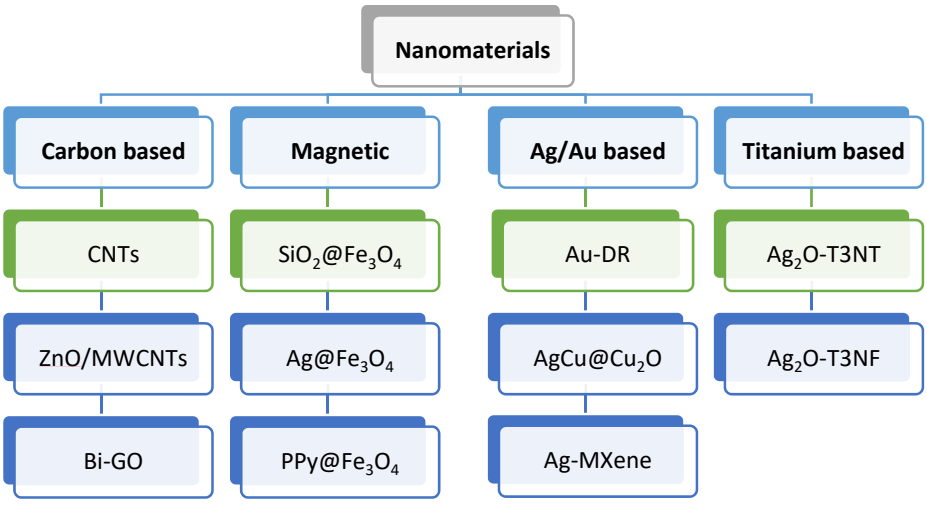

Figure 2. Nanomaterials applied for radioiodine removal from aqueous media.

sheet is made up of one carbon atom thickness. These nanotubes have been studied for the adsorption of iodine owing to their unique nano-tubular microstructure, radiation resistance, and chemical stability. They have shown an adsorption capacity of 1.536 mg/g for ^{131}I with an efficiency of 22.60%. This uptake is attributed to the high surface area and the large number of functional groups (-OH, -COOH, and C=O) present on the surface (4). CNTs are easy to synthesize and modify and provide a large external surface area with favorable stability. However, they are expensive, ecotoxic, and have low selectivity.

Multiwalled carbon nanotubes (MWCNTs) possess multiple concentrically connected nanotubes made of carbon. That is why, their diameter is greater than 100 nm. The nanocomposite containing ZnO and MWCNTs (ZnO/MWCNTs) is prepared by producing an arc in deionized water between graphite and zinc electrodes. ZnO/MWCNTs illustrated an adsorption capacity of 5 mg/100 ml at 25°C in 60 minutes at pH 5 for iodide ions. The removal efficiency reached as high as 94.7%; lowering the pH enhanced the adsorption due to the protonation of adsorption sites which attracted negatively charged iodide ions (17). The adsorption mechanism is mainly multilayered physical adsorption. However, the adsorption is lower than CNTs.

Graphene oxide (GO), a hexagonal planar film composed of carbon atoms and sp^2 hybrid orbitals, has diverse surface functional groups (e.g. –COOH, –OH, –COH, C=O, etc.). When functionalized with bismuth (Bi-GO), it demonstrated a removal capacity as high as 200-230 mg/g in 5 minutes at pH 6 for iodide and iodate ions owing to the formation of bismuth iodide and bismuth iodate. The removal efficiency approached 95% which is higher than other carbon-based nanomaterials investigated for radioiodine removal (18). However, GO has a disadvantage over CNTs in terms of time-consuming and pollution-generating synthesis.

Magnetic nanomaterials

The separation of nanomaterials post-radioiodine adsorption from water necessitates a time-consuming centrifugation process. Additionally, nanoparticles tend to agglomerate at higher salt concentrations leading to a loss of physiochemical properties. Magnetic nanoparticles such as magnetite and hematite have an intrinsic advantage of easy recovery from the solution by applying an external magnetic field. They also possess sur-

face efficiency, massive availability, and less waste generation. Among the magnetic nanomaterials, hematite nanofibers prepared by precipitation procedure show an adsorption capacity of 27 mg/g in 30 minutes at a pH 2 for iodide ions. The adsorption efficiency is ascribed to the protonation of adsorption sites (19). These hematite fibers though provide a low adsorption capacity but are economical to produce. In further studies with magnetic nanoparticles, they were functionalized with either silver or some organic material that has a good affinity for iodine. The functionalization procedure enhanced the adsorption capacity at the expense of cost.

Magnetite nanoparticles prepared by the coprecipitation method, coated with silica, and modified with imidazole pendants showed an adsorption capacity of 140.84 mg/g at pH 7 in 40 minutes with a removal efficiency of 98%. Imidazole is a five-membered aromatic molecule having two annular nitrogen atoms which have a chemical affinity toward iodide ions. The removal efficiency of these nanoparticles is attributed to this aforementioned affinity (20). In another study, magnetite nanoparticles coated with silver (Ag/Fe_3O_4) displayed an adsorption capacity of 847 mg/g in 60 minutes for iodide ion removal from water. Silver has a notable affinity toward iodide ions in water. It removes iodide ions either by adsorption or by forming precipitates of insoluble silver iodide. That is why Ag/Fe_3O_4 exhibited a removal efficiency of 94% with good recyclability and maintained performance even in competitive ions and a wide pH range (21). Magnetite nanoparticles encapsulated in the polypyrrole (PPy) matrix (Fe_3O_4@PPy) also demonstrated an iodine uptake of 1627 mg/g in 2 h at room temperature. This is the highest uptake among all nano-materials studied for the purpose as shown in Table 1. These particles provided an additional advantage of adsorbent regeneration on washing with ethanol. The adsorption is attributed to charged transfer from a lone pair of nitrogen of PPy to the antibonding molecular orbital of iodine (22). However, all these functionalized magnetic nanoparticles are expensive to synthesize.

Titanium-based Nanoparticles

The excellent stability under radiation, chemical, thermal, and mechanical conditions makes titanium-based nanoparticles suitable for radioiodine removal. They can

Table 1. Iodide ion (I^-) adsorption capacity and dynamics for all the nanomaterials discussed in the paper.

Nanomaterial	Adsorption Capacity (mg/g)	Adsorption Time (min)	Temperature (°C)	pH	References
CNTs	1.536	-	-	-	(4)
ZnO/MWCNTs	5	60	25	5	(17)
Bi-GO[a)]	230	5	-	6	(18)
Fe_3O_4	27	30	25	2	(19)
SiO_2@Fe_3O_4	140.84	40	25	7	(20)
Ag/Fe_3O_4	847	60	80	2-12	(21)
PPy/Fe_3O_4	1627	120	25	2-12	(22)
Ag_2O–T3NT	190	30	25	≥ 7	(23)
Ag_2O–T3NF	381	30	25	≥ 7	(24)
Au-DR	3.7 MBq	30	25	-	(25)
AgCu@Cu_2O	63.5	1440	25	3-10	(26)
MXene-PDA-Ag_2O_x	80	60	25	5	(27)
Mxene-AgNW	84.70	60	25	7	(28)

[a)]Bi-GO removes both iodide and iodate ions from the aqueous media.

also be easily synthesized under low-cost hydrothermal conditions from TiO_2 precursor. Moreover, Ag_2O has a good affinity for iodine ions. Titanate nanotubes (Ag_2O–T3NT) and nanofibers (Ag_2O–T3NF), when grafted with silver showed adsorption of 1.50 mmol/g (~190 mg/g) and 3 mmol/g (~381 mg/g), respectively with an efficiency of 90% for iodide ions in first 30 minutes. The adsorption is attributed to the formation of silver iodide on the surface of 1D nanostructures (23, 24). These nanostructures provided very fast kinetics and facile separation of the adsorbents from solution for disposal. However, some magnetic materials have also performed in the same range as evident in Table 1.

Metal and Metal-doped materials

Gold nanoparticles immobilized on dextran gel columns showed an adsorption efficiency of greater than 99% in 15 minutes due to the chemisorption of iodide ions on the gold surface; however, at high salt concentrations, they released the ions into the water. That's why, gold nanoparticles containing Deinococcus radiodurans R1 (Au-DR) were prepared by biomineralizing gold metal ions. Deinococcus radiodurans R1 is one of the most radiation-resistant organisms that can access the contaminated area without excavation and provide the advantage of cost-effectiveness. Au-DR nanoparticles were prepared by incorporating gold nanoparticles in bacteria cultures. These particles absorb more than 99% (3.7 MBq of ^{125}I) of the iodide ions from the solution in 30 minutes at room temperature. However, the material completely inhibits adsorption at high iodide ion concentrations (25).

Copper and copper oxide have also been reported to have a chemical affinity for iodide ions. That is why the affinity of copper, silver, and copper oxide for iodide ions is exploited in the succeeding study. Silver and copper dopped on copper oxide (AgCu@Cu_2O) were prepared by solvothermal method. These nanoparticles showed an adsorption capacity of 0.5 mmol/g (~63.5 mg/g) at room temperature in the first few hours. The iodide ion uptake is attributed to CuI and AgI forming on the surface of Cu_2O nanoparticles (26). However, the preparation of the compound needs a lengthy procedure to optimize silver and copper concentration on the nanoparticles.

MXene, a 2D nanomaterial having layered titanium carbide or nitrides with diverse surface functional groups, is also a favorable choice on account of its resilience in radiation environments. Also, silver and silver oxide have a remarkable affinity toward iodide ions in water as mentioned in the previous sections. When MXene was functionalized with polydopamine and silver oxide (MXene-PDA-Ag_2O_x), it yielded an iodide adsorption capacity of 80 mg/g with an 80% efficiency at pH 5. The initial 60 minutes showed a faster uptake (27); however, the adsorption capacity decreased with the increase in temperature and pH. The MXene decorated with AgNW also exhibited a removal efficiency of 84.70 mg/g under diverse conditions such as pH from 2 to 12 and in the presence of competitive ions. The adsorption in both cases is attributed to the formation of AgI (28). However, the minor increase in adsorption capacity in the case of nanowires is because of the tubular morphology of nanowires.

The above discussion points out that most nanomaterials have shown impressive radioiodine removal efficiency in diverse and harsh laboratory environments. However, the highest uptake reported on nanoparticles that are not supported on column or membrane is 1627 mg/g for PPy/Fe_3O_4 and the fastest uptake is shown by bismuth functionalized graphene oxide (Bi-GO) which adsorbed 230 mg/g of iodide ions from aqueous media only in 5 minutes. Additionally, Ag/Fe_3O_4 nanoparticles maintained their adsorption capacity in the most diverse temperature and pH conditions. Hence, while diverse nanomaterials excel in radioiodine removal, certain types possess inherent advantages over others as illustrated in Table 1.

Conclusion

In conclusion, carbon-based nanomaterials particularly CNTs and GO have shown promising removal capacities for radioiodine removal despite their high cost and ecotoxicity. On the other hand, magnetic nanoparticles have the intrinsic benefit of easy synthesis and recovery under the action of the magnetic field. Functionalizing these nanoparticles with silver or organic compounds enhances their removal efficiency dramatically but at an expensive cost. Additionally, titanium-based nanoparticles owing to their stability and easy synthesis present avenues for the purpose but their removal efficiencies are significantly lower than other nanoparticles. Furthermore, MXene can potentially remove iodine from aqueous media but it is associated with ecotoxicity. Thereby, most of these nanomaterials have the potential to translate into industrial applications with their own sets of advantages and disadvantages but it is necessary to research in the field to optimize their efficacy and resolve the associated challenges.

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