

**Adsorbents used for removal of mercury from aqueous solutions: A review**

**Abstract**

This article looks at the adsorbents which are used to eliminate mercury in solutions. Researchers have addressed removing mercury as a pollutant from the wastewaters of several industries. Heavy metals are being removed from wastewater through adsorption on activated carbon, which is becoming additional popular. Despite the fact that commercial activated carbon is the ideal adsorbent for pollutant elimination, its extensive usage is limited because of its high cost, encouraging researchers to explore for alternative effective and low-cost adsorbents. The goal of this study is to bring together diverse evidence on an extensive variety of potentially effective and low-cost mercury adsorbents. These include activated carbon, polymers, nanoparticles, and low-cost adsorbents. For the remediation of water from mercury, polymers, as well as nanoparticles, which are very effective adsorbents, can be employed. According to a literature review of the most recently published research, polymers and nanoparticles have exhibited exceptional mercury removal capabilities.

**Key Words:** - Mercury, heavy metal, removal, wastes, Adsorption capacity.

**1. Introduction**

For the past few decades, water contamination caused via the dumping of wastes comprising heavy metals has been a global apprehension. Some heavy metals are well known to be detrimental to humans, causing toxic effects and disrupting healthy natural settings. Mercury was one of the first metals to be discovered, and humans have been using its compounds for ancient times. Mercury and its derivatives, which have exceptional chemical and physical properties, are global pollutants. Mercury poses a threat even at very low concentrations because it accumulates in the food chain. Mercury has a unique property in that it absorbs quickly into biological tissues and takes a long time to leave them. Mercury pollution is mostly caused by effluents

from the chloralkaline, pulp and paper, oil refining, electrical, rubber processing, and fertilizer industries [1]. Another substantial source of mercury emissions into the environment is flue gases from charcoal combustion systems used in electricity generation [2, 3].

Acute mercury poisoning can induce chest pain, difficulty breathing, vomiting, diarrhea, fever, a metallic taste in the mouth, and a rash on the skin. Long-term exposure can cause tremors, limb weakness, a loss of appetite, excessive shyness, irritability, headaches, and memory loss. Mercury has an impact on the central nervous system, pulmonary-renal functioning, and chromosomes [4]. Mercury has a strong affinity for protein binding, and it primarily impacts the renal and neurological systems. Mercury poisoning, according to research, is particularly detrimental to developing fetuses and children under the age of four, as it interferes with appropriate brain development. Before it can be recycled or released into the environment, mercury must be removed from the wastewater [5].

Several workers have considered the elimination of mercury from wastewater by using various removal strategies, including coagulation [6, 7], photocatalysis [8-10], solvent extraction [11], and ion exchange [12-14]. These technologies, however, have limitations for instance the wide usage of chemicals, low removal efficiency at low concentration levels, and lack of selectivity [15-18]. Adsorption and membranes are two competing separating units that achieve high removal percentages and high selectivity rates at low concentration levels. Adding functional groups like thiols, which operate as a strong mercury ion binding site, can improve both approaches, according to Alberni et al. However, waste disposal and fouling are the two most common challenges associated with adsorption and membrane separation. The adsorption method is a potential option because it offers a number of benefits over membrane technologies, including cheaper capital and operating costs, ease of operation, and the ability to remove hazardous substances using a variety of solid media [19]. For decontaminating water, adsorption [20-23] is a well-equilibrium separation method. In terms of initial cost, design flexibility and simplicity, and operational ease, and sensitivity to harmful impurities, adsorption outperforms competing water recycling technologies. There is no creation of potentially hazardous chemicals as a result of adsorption. Toxic metals have been removed using adsorbents

for instance clays, zeolite, natural products, activated carbon, polymers, nanoparticles, low-cost materials, and others [24-28].

The technical feasibility of many common adsorbents for mercury and their derivatives removal from water and wastewater is discussed in this review paper. The primary goal of this study is to provide a concise overview of recent research on the usage of activated carbon, polymers, nanoparticles, low-cost materials, and other adsorbents. The authors suggest that the maximum capacity be interpreted as a set of conditions rather than reported adsorption capabilities. For details on experimental circumstances, the reader is strongly recommended to consult the original research articles.

## **2. Adsorbent's literature**

### **2.1 Activated carbon**

Nearly any carbonaceous material can be employed as per a precursor for the manufacturing of carbon adsorbents [29], but coal is the maximum usually used precursor for the preparation of activated carbon due to its widespread availability and inexpensive cost. Coal, a blend of carbonaceous and mineral components, is formed when plants disintegrate. The novel vegetation and the extent of the physical-chemical changes that occur after deposition determine the sorption properties of each coal.

Heavy metals are removed from natural water and wastewaters, commercial activated carbon is a well-known adsorbent. However, its high cost prevents it from being used as an adsorbent. As a result, there is an increasing demand for low-cost activated carbon prepared from less expensive and locally available agricultural waste [29]. The two most popular methods for creating activated carbons are physical and chemical activation. The physical activation approach includes carbonization of the raw material and activation at a high temperature in a carbon dioxide or steam atmosphere. [30]. Chemical activation is a well-known method for producing activated carbon that has recently been the subject of several studies due to its major advantages over "physical activation." Carbonizing the raw material and then activating it at a high temperature in a carbon dioxide or steam atmosphere is the physical activation process. The precursor is impregnated with a chemical agent and then pyrolyzed in a chemical activation process. The pyrolysis process produces a material with substantially higher carbon content and a more organized structure. The porosity

develops dramatically when the chemical agent is removed via heat treatment. Chemical activation has several advantages to physical activation, one of which is the quickest time it takes to complete the process [31]. The adsorption capacities of mercury adsorbed by activated carbons derived from various materials are reported in Table 1 to determine the best conditions, methods, and raw materials required for producing activated carbon with effective adsorptive properties toward mercury.

**Table 1: Capacity of adsorption for selected activated carbons**

No	Adsorbents	Adsorption capacity (mg/g)	Ref.
1	Ceiba pentandra hulls were used to make activated carbon.	25.88	[5]
	Activated carbon made from the hulls of Phaseolus aureus	23.66	
	Cicer arietinum-derived activated carbon	22.88	
2	Carbon generated from fertilizer waste as activated carbon	654.0 at 27 °C 371.1 at 45 °C 72.4 at 65 °C	[32]
3	Antibiotic waste activated carbon	129	[33]
4	Activated Carbon Made from Coconut Shells	15.20	[34]
5	Furfural produces activated carbon.	174	[35]
6	Activated carbon made from coirpith, a waste agricultural solid by-product.	154	[36]
7	Made from sago waste, activated carbon	55.6	[37]
8	Palm oil activated carbon empty fruit bunch	52.67	[38]
9	Activated carbon impregnated with sulfur	800	[39]
10	Mixed recyclable garbage activated carbon	27.6	[40]
11	Activated carbons that have been sulfurized	578 at 65 °C	[41]
12	Activated carbon made from sawdust	182.2 at 30 °C	[42]
		201.7 at 40 °C	
		216.3 at 50 °C	
		232.9 at 60 °C	
13	H <sub>3</sub> PO <sub>4</sub> produces activated carbon.	160	[43]
14	Activated carbon made from pistachio wood waste	202	[44]
15	In simulated landfill leachate, modified activated carbon from peat soil was used.	114	[45]
	In simulated landfill leachate, modified activated carbon of coal was used.	102	

16	Magnetic activated carbon with thiol functionalization	366.3	[46]
17	Carbon activated with poly ethylenimine	16.39	[47]

Table 1 shows that activated carbon generated from fertilizer waste has a suitable capacity for mercury adsorption (654.0 mg/g at 27°C) [32]. The greater surface area (629 m<sup>2</sup>/g) and negligibly small quantities of silica and ash in this activated carbon explain its higher adsorption capability. This indicates that the raw materials, activation agent, and experimental conditions used to produce this activated carbon were suitable. Table 1 also demonstrates that at 400°C, sulfur impregnation of activated carbon produced the best adsorbent, with an adsorption capacity of 800 mg/g for Hg(II) [39]. This suggests that sulfur impregnation considerably enhanced the adsorption capacity of activated carbon for Hg(II). The chemical interaction between sulfur atoms and functional groups on the surface of virgin activated carbon (e.g., carbonyl, carboxyl, phenol, and lactone) produces sulfone, sulfoxide, and thiophene, which serve as the main mercury adsorption active sites [39].

## 2.2 Polymers

Due to the availability of various functional groups, several polymer-based adsorbents have previously been employed for heavy metal adsorption from contaminated water. Pure polymers, on the other hand, have a number of drawbacks, including low stability and the separation of adsorbents from wastewater after adsorption treatment, particularly when powdered. If the used adsorbent can be efficiently recovered, it can be regenerated and reused, resulting in a lower capital investment [48].

Hg sorbents have been proposed using a variety of polymer sorbents that immobilize sulfur-containing functional groups, such as thiol, thiocarbamate, thiourea, thiazole, and thiazoline(II) [49-54]. However, because heavy metal sorption affects the sorbent's sorption capacity and effectiveness, the presence of high amounts of these heavy metals in wastewater could reduce the efficacy of Hg(II) removal using the sorbent. Based on this idea, polymer sorbents with excellent Hg(II) selectivity are being investigated in a variety of wastewater treatment applications. Furthermore, because Hg(II) and other heavy metal-containing wastewater is often acidic, polymer sorbents' ability to remove Hg(II) under acidic circumstances is favorable [55].

Prior to ultrafiltration, water-soluble metal-binding polymers are included in polymer-assisted ultrafiltration (PAUF), a similar process for eliminating metal ions. The introduction of complex polymers, which produce vast complex entities that increase the amount of the solute to be retained, makes filtration easier [56].

Porous organic polymers have become a hot topic in recent years due to their wide range of applications, including gas storage, molecular separations, heterogeneous catalysis, pollutants adsorption, and so on [57-59]. They are highly designable solid supports with synthetic variation as the key benefit [60-61].

In normal processes for their production, the employment of costly noble metal catalysts or powerful Lewis acid catalysts is frequently necessary [62]. As a result, efficient design and catalyst-free synthesis of novel functional porous polymers from simple, inexpensive, and easily available chemical monomers remains a difficult and essential research topic in polymer chemistry [63]. Triazines, especially melamines, have shown great potential in the burgeoning fields of supramolecular [64] and dendrimer [65] chemistry via donating and accepting hydrogen bonds, metal chelation, and pep interactions. Melamine (MA) is a 66 percent nitrogen triazine monomer widely utilized in the plastic, pharmaceutical, ornamental, and paper industries. It seems to be a suitable choice for being used as a raw material to make N-rich materials (like carbon nitride and N-enriched carbons) with weak basic functionalities [66-67], which have a variety of applications, including metal-free catalysis [68], CO<sub>2</sub> adsorption [69], supercapacitors, and other industrial processes. Because of its high stability and N functionality, the s-triazine ring has recently emerged as a remarkable element in the production of porous polymers. The porous covalent triazine-based framework (CTF), which is a good catalytic support for metal particles with high surface areas and remarkable thermal and chemical durability [63, 70-71], has received a lot of attention. However, until recently, the MA was exclusively employed as a monomer to make porous polymers without the usage of fussy templates. Table 2 lists some of the polymers that have recently been employed to remove mercury from wastewater.

**Table 2: Adsorption capacities for chosen polymers**

No	Name of adsorbent	Adsorption capacity (mg/g)	Ref.
1	Microporous polymer with a high sulfur content	595.2 mg/g	[72]
2	Porous organic polymers based on triazine	229.9 mg/g	[73]
3	Magnetic porous organic polymers with thiol functionalization	910 mg/g	[74]
4	Polymeric resin with magnetic properties	188.4 mg/g	[48]
5	Porous organic polymers with thiol/thioether functionalization	180 mg/g	[75]
6	Sulfur-containing nitrogen-rich organic polymer with a hierarchically porous structure	3106 mg/g	[76]
7	Polythioamides complexing membrane poly(vinylalcohol)/poly(vinylimidazole)	700-850 mg/g	[77]
8	Polymeric resin with magnetic properties	853 mg/g	[78]
9	Melamine-based porous polymer	1172 mg/g	[79]
10	Polyaniline/attapulgitite composite	909.1 mg/g	[80]
11	Starch-g-Poly-(N-methylacrylamide-co-acrylic acid)	11.0 mg/g	[81]
12	A novel series of cross-linked polydithiocarbamates	22,1 mg/g	[82]
13	A novel polymeric magnetic boehmite nanocomposite (boehmite@Fe <sub>3</sub> O <sub>4</sub> @PLA@SiO <sub>2</sub> )	36.94 mg/g	[83]
14	MoS <sub>2</sub> -nanosheet-decorated PVDF composite	578 mg/g	[84]
15	Porous sulfur copolymers	371.3 µg/g	[85]
16	MoSe <sub>2</sub> nanosheet	208.3 mg/g	[86]
17	Amide functionalized cellulose from sugarcane bagasse	178 mg/g	[87]
18	Thiol-functionalized polymer-coated magnetic particles	80.3 mg/g	[88]
19	A dendrimer-grafted polyacrylonitrile fiber in fixed-bed column	227.6 mg/g	[89]
20	Magnetic composite adsorbent based on starch/polyethyleneimine	244.9 mg/g	[90]
21	Magnetic nanomaterial with bifunctional groups and core-shell	504.3 mg/g	[91]
22	Thiophenol-thiophene polymer	62.5 mg/g	[92]

23	Microporous functional silica-polymer sponge-like composite	582 mg/g	[93]
24	New network polymer functionalized magnetic-mesoporous nanoparticle	515.5 mg/g	[94]
25	A new dendrimer-functionalized magnetic nanosorbent	90 mg/g	[95]
26	Chitosan functionalized by amino-terminated hyperbranched polyamidoamine polymers	526.3mg/g	[96]
27	Alginate, pectate and polygalacturonate calcium gel beads	280 mg/g (Alginate beads) 300 mg/g (PGA beads) 340 mg/g (Pect beads)	[97]
28	New modified poly(vinylamine)-gels	248.8 mg/g	[98]
29	Polyaniline-Fe <sub>3</sub> O <sub>4</sub> silver diethyldithiocarbamate nanostructures	222.2 mg/g	[99]
30	Cryogels	742 mg/g (AAC cryogel) 676 mg/g (SAC cryogel)	[100]
31	Dithiocarbamate functionalized-magnetic nanocomposite	109.5 mg/g	[101]
32	Hyperbranched polyethylenimine functionalized carboxymethyl chitosan semi-interpenetrating network composite (HPFC)	1594 mg/g	[102]

In the comparison between the performance of activated carbons (Table 1) and the polymers in Table 2 for the adsorption of mercury, it will be seen that the former is significantly better than the latter due to the availability of different functional groups [48]. Table 2 also shows that thiol-functionalized magnetic porous organic polymers [74], sulfur-containing nitrogen-rich robust hierarchically porous organic polymers [76], melamine-based porous polymers [79], polyaniline/attapulgite composite due to its amine and imine functional groups [80], and due to the strong non-covalent interaction of the ligand S and N lone pairs with Hg<sub>2</sub>, sulfur-containing nitrogen-rich robust hierarchically porous organic polymers A sulfur-containing nitrogen-rich strong hierarchically porous organic polymer [76] has the highest adsorption capacity (3106 mg/g).

## Nanoparticles

Due to their unique physicochemical qualities, such as large surface area, high adsorption capacity, quick diffusion rate, and changing surface functionalities, nano-scale materials have gotten a lot of interest [103, 104]. Similarly, metal nanoparticle (NP) materials that are highly distributed and ultrafine have been widely researched as tiny scavengers for heavy metal ion removal from polluted water [105-108]. Due to their increased surface area and number of exposed active sites, most of these metal NPs were found to have significant effectiveness for heavy metal removal when compared to the bulk. Furthermore, when metal NPs are connected to adequate supports, they perform better during reactions [109-111].

Metal NPs, on the other hand, demonstrate high aggregation in actual environmental applications, which hinders their effective use and catalytic activity [112]. Hybrid composites are typically created to anchor NPs and obtain very stable and distributed metal NPs to tackle this problem. Activated carbons [113], sol-gel mesoporous silica [114], amorphous porous organic polymers [115], metal oxides [116], graphene [117], and metal-organic frameworks (MOFs) [118] have all been proposed as supporting matrices. Inorganic porous materials, on the other hand, have limited reaction space due to heavy hazardous metals' limited access to their porous channels. Other mesoporous or macro-porous materials created using templates are prone to collapsing during use. Although stability in acidic aqueous solutions is not assured for many MOF materials, when used for heavy metal pollution cleanup, MOF materials can expose large surface areas and many open channels. Another potential stumbling hurdle to NP utilization is their volatility in acidic solutions. The environment and humans appear to be more affected by exposure toxicity, restricting the usage of NPs in next-generation technologies [119, 120]. As a result, sustained use of highly spatially distributed metal NPs in acidic water decontamination applications remains a concern.

Nanoscale metal oxides, particularly magnetic nanoparticles, have many advantages, including high surface area-to-volume ratios, fast extraction dynamics, high extraction capacity, and a specific affinity for heavy metal adsorption from aqueous systems. Magnetite is a viable alternative due to its adsorption technique combined with magnetic separation [121], which allows the adsorbent and adsorbate to be easily

separated from the aqueous phase using an external magnetic field. Due to the presence of hydroxyl groups on the surface of iron oxide nanoparticles, magnetic nanoparticles as a solid phase adsorbent can modify the surface, providing a diverse synthetic handle for the attachment of various functions [122]. Table 3 lists recent nanoparticles utilized as adsorbents and their adsorption capabilities.

**Table 3: Some nanoparticles used to remove mercury have adsorption capabilities.**

No	Name of ads	Adsorption capacity (mg/g)	Ref.
1	Ag nanoparticles anchored in covalent organic frameworks	113	[123]
2	mercaptoamine-functionalized silica-coated magnetic nano-adsorbents	355	[124]
3	hyperbranched and multi-functionalized dendrimer modified mixed-oxides nanoparticles	3232	[125]
4	Ag supported on nano mesoporous silica	42.89	[126]
5	magnetic iron oxide nanoparticles modified with 2-mercaptobenzothiazole	0.59	[127]
6	di-thio grafted on magnetic mesoporous silica nanoparticles	538.9	[128]
7	thiol-functionalized magnetic nanoparticles	344.82	[129]
8	magnetic nanoparticles coated with amino organic ligands and yam peel biomass	a. MNP-APS (426.50) b. MNP-P (278.63) c. MNP-YP (215.6)	[130]
9	covalent triazine framework encapsulated $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> nanoparticles	165.8	[131]
10	cadmium sulfide nanoparticles doped in polycaprolactam nanofibers	162	[132]
11	Pumice-supported nanoscale zero-valent iron	332.4	[133]
12	functionalized mesoporous silica nanoparticles with the amine compound	a. KIT-6 (38) b. DA-KIT-6 (50)	[134]
13	Silver/quartz nanocomposite	376.3	[135]
14	Gold-Functionalized Fe <sub>3</sub> O <sub>4</sub> Magnetic Nanoparticles	79.59	[136]
15	EDTA functionalized graphene oxide nanoparticles	390.9	[137]
16	magnetic graphene oxide	71.3	[138]

Because of their higher surface area and variable surface functional groups, most nanoparticle materials have acceptable adsorption capacities (Table 3), but hyperbranched and multi-functionalized dendrimer modified mixed-oxides nanoparticles have the highest capacity for mercury adsorption from aqueous solution (3232 mg/g). This is due to the adsorbent nanoparticles' diverse functional groups and hydrophilic reactive sites [125].

#### 2.4 Low-cost materials

In recent years, clays, biomass, agricultural, and industrial residuals have all been employed to generate low-cost adsorbents [140-144]. Such adsorbents include coal fly ash (CFA), naturally occurring zeolites, and synthetic zeolites made from low-cost starting materials such as Si and Al [145-150]. For example, Liu et al. [151] created a hybrid mesoporous alumino-silicate sieve (HMAS) out of fly ash. After then, the mixture was successfully impregnated with zeolite A precursor. When various parameters, such as pH and temperature, were evaluated, high effectiveness for mercury removal was established. On the other hand, cost-effectiveness was not taken into account. CFA is a by-product of coal combustion in power plants, and several recent research have proposed CFA reuses [152]. CFA is produced in millions of tons per year all over the world. Due to its fine structure and hazardous components, CFA production is currently rising, posing a severe environmental threat [153, 154].

The effectiveness of CFA in eliminating mercury from flue gas has been demonstrated [155-159]. The unburned carbon contained in fly ash has been found to be the most effective particle for trapping mercury in coal-fired power plants in many investigations [155]. This could be the secret of CFA's success in removing mercury ions from liquid medium. However, because additional heavy metals and hazardous species trapped in the CFA structure can be released into the liquid solution during the adsorption process, its adoption can be difficult.

As a result, while CFA removes mercury from effluent, other harmful heavy metals like As and Cr may be released into the environment. Furthermore, as compared to other adsorbents, raw CFA has a low adsorption capacity [160-161]. CFA's adsorption qualities can be improved while the problem of leaching is reduced, according to new

research. The most frequent method for altering CFA is to convert it into zeolites, which is effective at enhancing heavy metal removal [157, 161, 162]. Table 4 shows the adsorption capacity of certain low-cost materials that have been utilized to remove mercury from wastewater.

**Table 4: adsorption capacity for some low-cost materials used for mercury removal**

No	Name of ads	Adsorption capacity (mg/g)	Ref.
1	Lignin xanthate resin–bentonite clay composite	438.75	[163]
2	<i>Lactarius acerrimus</i> macrofungus	134.9	[164]
3	A low-cost adsorbent from coal fly ash	0.44	[165]
4	agroindustrial waste adsorbents	a. CSB 13.55 b. SBZ 11.47	[166]
5	Functionalized three-dimensional (3D) graphene composite	1000	[167]
6	coal gasification slag	1.96-2.27	[168]
7	<i>Lemna minor</i> powder	28.2	[169]
8	by powdered leaves of castor tree ( <i>Ricinus communis</i> L.)	37.2	[170]
9	eucalyptus bark	33.11	[171]
10	banana peels	0.75	[172]
11	amide functionalized cellulose from sugarcane bagasse	178	[173]
12	date pits	a. RDP (282) b. SMRDP (280) c. SIMRDP (90)	[174]

It can be seen from Table 4, that most low-cost adsorbents have insufficient performance for the adsorption of mercury compared with the other types of adsorbents like activated carbon, polymers, and nanoparticles. Among all these adsorbents, only the functionalized three-dimensional (3D) graphene composite due to the –SH functional group present on its surface has a considerable adsorption capacity (1000 m g/g) [167].

### 3. Conclusions

This review attempts to cover a wide range of adsorbents for the reader to obtain a better knowledge of the best types of adsorbents used to remove mercury from wastewater. Less costly, readily available, and effective materials should be employed to remove mercury from aqueous solutions. Few attempts appear to have been undertaken to compare the cost and performance of various adsorbents. To encourage the large-scale usage of adsorbents, this issue must be researched further. The broad use of effective and low-cost adsorbents in wastewater treatment applications is strongly advised nowadays because of the paucity of the reliable pricing information. If adsorbents remove mercury effectively at a cheap cost, they can be accepted and broadly employed in industries to cut costs while simultaneously increasing profitability. Effective and low-cost adsorbents, without a question, hold a lot of promise for future commercial applications. The surface area, porosity, and surface functional group of the adsorbent all have a role in mercury absorption, according to the literature. Mercury adsorption needs more research in the areas of modeling and adsorbent renewal. Most of the research covered are batch processes, which provide a foundation for the design of continuous flow systems with industrial applications on a commercial level. More research is needed to make the process functional and cost-effective on an industrial scale, with a particular focus on adsorbent renewal. Finally, we'd like to touch on the adsorption method' zero-waste technique for mercury removal from water and wastewater.

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