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REVIEW

Metal Oxide-Based Adsorbents for Removal of Mercury in Aqueous Media: A Mini-Review

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Abstract
Mercury-related products pose a serious environmental and health threat due to increasing industrialization, inadequate removal treatments, and lenient regulations, making mercury removal critically important. Metal oxides are showing great promise for removing mercury from aqueous solution because of their chemical stability, high surface area, and affinity for mercury ions. These oxides enhance mercury adsorption through interactions between mercury and their active sites. This review discusses recent advances in the synthesis and application of metal oxide-based adsorbents, emphasizing their effectiveness in mercury removal and potential for mitigating environmental contamination. Additionally, recommendations are provided to enhance mercury removal efficiency by elucidating the fundamental adsorption mechanisms.

Keywords Mercury · Adsorption · Metal oxides · Aqueous

1 Introduction

Heavy metal pollution in the biosphere can be attributed to the exponential increase in industrialization and urbanization globally [1]. Many heavy metals exist naturally in the earth's crust. The biochemical balance and geochemical cycle of such heavy metals change substantially due to geochemical changes and increasing inappropriate anthropogenic activities [2]. They have been reported to be toxic above a certain threshold and their toxicity depends on factors like the amount of dosage, age, health status, and the time at which an individual is exposed to a particular heavy metal [3, 4]. The scientific community has been very concerned with the environmental effects of heavy metals on the well-being of humans and the environment for a long time now [5]. Such heavy metals are cadmium (Cd), arsenic (As), lead (Pb), nickel (Ni), cobalt (Co), and mercury (Hg) among others [6].

Mercury is dense, relatively stable, and also has high surface tension [7]. Hg exists in seven different stable isotopic forms with the following percentages of abundance corresponding to the earlier given atomic weight: ^{196}Hg (0.155(4)%), ^{198}Hg (10.038(10)%), ^{199}Hg (16.938(9)%), ^{200}Hg (23.138(6)%), ^{201}Hg (13.170(12)%), ^{202}Hg (29.743(9)%), and ^{204}Hg (6.818(6)%). Among all these isotopes of Hg, ^{202}Hg is the most abundant form [8]. Mercury has been utilized in florescent lamps, batteries, pesticides, pigments, chemical catalysts as well as in glass Hg thermometers. However, serious Hg pollution has occurred from its environmentally unsound treatments [9]. So, Hg has been labeled as a global contaminant because of its deleterious effects on human health as well as other organisms in the environment [10]. The incident of Hg poisoning that occurred in Japan in the 1950s when the chemical substance was discharged into Minamata Bay by the Chisso Corporation began the

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awareness of the health effects of Hg pollution. This occurrence led to the bioaccumulation of methylmercury (MeHg) in fish, which consequently caused health challenges as well as the death of a lot of people who consumed the fish [11]. Similarly, severe MeHg poisoning happened in the 1970s in rural Iraq when bread was produced from wheat seeds that had been sprayed with fungicides containing organic Hg and fed to people [12, 13]. The Hg poisoning episodes that occurred in Japan and Iraq are the two most commonly discussed Hg pollution in the literature owing to their severity.

The most commonly employed conventional technologies for removing Hg ions from water include the ion exchange method [14], liquid extraction method [15], chemical precipitation method [16], metal reduction, electrolytic method [8, 14], etc. However, many of these methods suffer significant limitations, including high energy demands, excessive energy consumption, operational costs, low removal efficiency, and lack of selectivity [17]. Currently, the adsorption method is the most famous and the best owing to its cost-effectiveness and ease of operation [18, 19]. The adsorption method involves the interaction between the adsorbent and adsorbate via electrostatic attraction, van der Waals force, chemical bond, and so on [9]. In this case, the main aim of removing the Hg ion is achieved via the adsorption. The efficiency of the latter greatly is strongly dependent on the constituents, morphology, structure, outstanding adsorption capacity, and the renewability of the adsorbent. Many reviews have been published on the removal of mercury using non-carbon materials, but reviews on the use of metal oxides for mercury removal from aqueous solutions are scarce.

Recently, numerous metal oxide (MO) materials have been synthesized and utilized for the removal of mercury from aqueous solutions, where they demonstrated outstanding physical and chemical properties. MOs have been extensively studied to gain insights into various physical and chemical processes due to their powerful electron-electron interaction, as well as their compositional simplicity and stoichiometric diversity [20]. In addition, MOs can be enhanced through chemical and structural modifications, doping of hetero-atoms, or synthesis of nanocomposites, which make them more powerful and therefore highly investigated [21]. They have also been found to possess remarkable recycling and regeneration rates, and good stability, making them highly effective for different applications [22]. Due to these merits, MOs have been utilized for various purposes like heavy metals removal, poisonous gas sensing, textile coating for wearable electronic devices, biomedical applications, and photocatalytic degradation of organic pollutants [23]. Some examples of metal oxide adsorbents with remarkable removal mercury efficiency include metal-doped spinel oxides [24] and supported metal oxide nanoparticles [17, 25], This investigation was motivated by the adverse effects of mercury on human health and the environment, coupled with the proven effectiveness of metal oxides in treating mercury-contaminated media. This study aims to review the existing literature on the use of metal oxide adsorbents for the removal of mercury from aqueous solutions, addressing a notable gap in the research. In this review, studies on the removal of mercury from aqueous media are summarized, highlighting the preparation strategies of the recently developed metal oxides, adsorption performances, and effects of process parameters on removal efficiency. The information presented in this study aims to provide the scientific community with a robust and clear understanding of the roles of metal oxides in the adsorption-based removal of Hg ions, thereby guiding future research directions.

1.1 Fundamental Forms of Mercury

Mercury can be found in three different forms which are: (a) elemental mercury, often known or metallic Hg (Hg^0), inorganic mercury (e.g. mercuric chloride, $HgCl_2$), and organic mercury compounds (i.e. methylmercury, MeHg; ethylmercury, EtHg; and phenylmercury, PhHg) [26, 27] The three fundamental forms of Hg are shown in Fig. 1. These three forms of Hg are all inimical to humans, even though their absorption, how they are metabolized, and primary target organs are entirely different [28]. Mercury can be determined in human biological specimens such as blood, urine, hair nails, and others. Human urine has been found to reflect the body's excretion of elemental and inorganic Hg while the blood total Hg estimation shows all types of Hg circulating in the blood, including MeHg, the most common form of organic mercury [28].

1.2 Routes of Exposure to Mercury

Humans could be exposed to Hg via respiratory tracts, digestive tracts [29], and absorption through the transcutaneous process and these are illustrated in Fig. 2 [30]. The main two routes responsible for Hg exposure are occupational contact and dietary intake. Occupational contact majorly involves the exposure of humans to Hg^0 (i.e. elemental mercury) in Hg-related industrial processes such as Hg catalysts at chloralkali plants, and Hg or small-scale gold mining by inhaling gaseous Hg^0 or dust forms of Hg [31]. The most prevalent way that humans are exposed to mercury is through food consumption. The combined risks of mercury from eating fish, fruits, and tubers were higher than what was considered tolerable, without constituting carcinogenic risk to the health of highly exposed consumers. This is a toxicant that, via the food chain, can bioaccumulate and grow in aquatic environments, thereby causing high MeHg concentrations

Fig. 1 Forms of mercury and its reservoirs in human

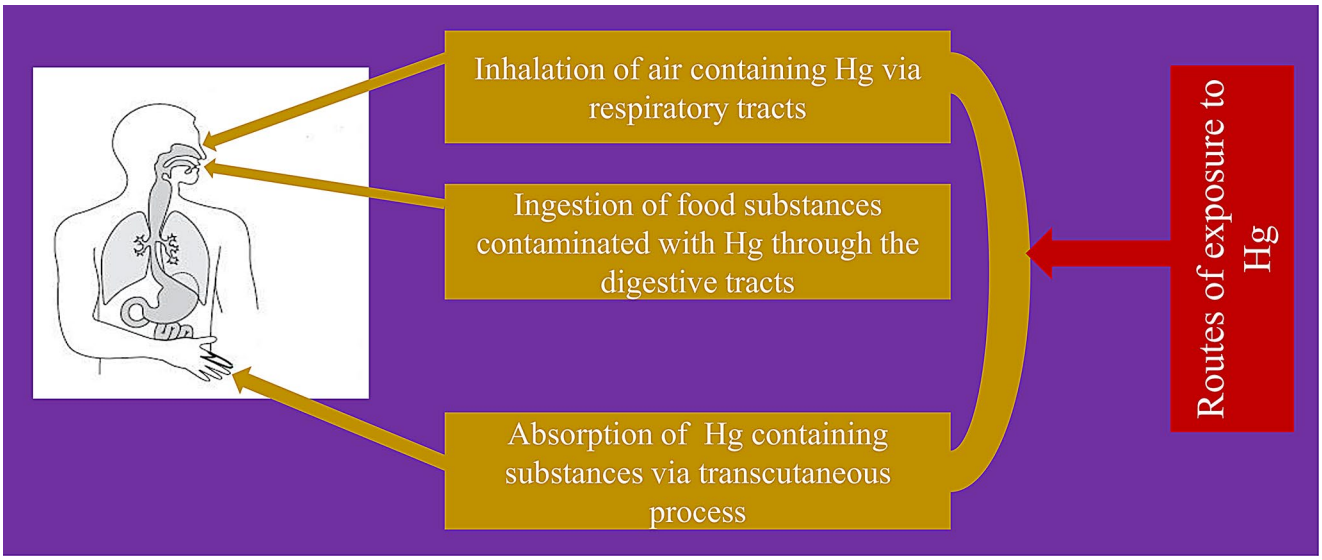

Fig. 2 Routes of exposure to mercury

at high tropic levels in fish [32]. So, the consumption of fish and seafood contributes significantly to the exposure of humans to MeHg [33, 34]. Furthermore, rice consumption has been reported recently to be another pathway through which humans are exposed to MeHg [35].

1.3 Sources of Mercury

The sources of Hg in the environment can divided into two main categories: (a) natural sources and (b) anthropogenic sources [1, 36]. Volcanic eruption, degassing from soils, weathering processes of the earth's crust, volatilization from the water surfaces, and forest fires have in no measure contributed to the natural sources of Hg [36]. Volcanoes and forest fires are the natural sources of mercury. It is determined that mercury has a residence duration of 0.8–1.7 years in the atmosphere. This metal has a quicksilver color look when it is liquid at room temperature and turns into vapor when exposed to environmental conditions. Although elemental mercury is not frequently found in the environment, it can be recovered from cinnabar ores [37]. According to United States Environmental Protection Agency (USEPA) estimates, the annual global Hg emissions from both natural and anthropogenic sources are approximately between 5,000 and 8,000 metric tons per annum [38].

Gassing of mercury during dental amalgamation, intake of contaminated ash, or occupational exposure are the main sources of Hg contamination in water [1]. In addition, mining, smelting, burning of waste, and coal ignition are the primary anthropogenic activities that contribute significantly

to water contamination with Hg [39]. Mercury contamination in the environment was found in a nearby pesticide industry somewhere in China [40]. The incineration process of municipal and medical wastes was also reported to have contributed to the high concentration of Hg in the environment [41]. According to a report by the USEPA, small-scale gold mining and coal combustion have contributed 38% and 21% respectively of Hg ingression in the environment, globally [36, 38] Also, non-ferrous metals production and cement production globally made up 15% and 11% respectively of Hg in the environment [38]. The major sources of Hg in the environment are depicted below (Fig. 3). Table 1 displays different forms of mercury adsorption from aqueous media by metal oxide adsorbents.

1.4 Consequences of Mercury on Human Health

Owing to the persistence and cosmopolitan nature of Hg, humans are usually exposed to it through some of the previously discussed routes. It has been reported that the reproductive health of both males and females can be altered due to exposure to Hg. High concentrations of Hg in blood and hair were found to be responsible for subfertility or infertility status in males [52, 53] Evidence also exists whereby Hg was linked with erectile dysfunction [54]. Mercury exposure causes an imbalance in the female hormonal system that leads to infertility in women by increasing prolactin secretion. This is synonymous dopamine effect at the midbrain level [53].

Mercury is also posited to be inimical to the central nervous system (CNS). Cognitive impairments, mostly in memory, attention, and psychomotor functioning have been found in people who were exposed to Hg vapour [55]. Cognitive deficits and losses in sympathetic autonomic activity among patients occupationally exposed to Hg vapor have also been reported [56]. Although, it is not all reported studies that found changes in the same indicators [57] High concentrations of Hg were detected in the brain tissues of individuals who died more than one decade after the end of their exposure to Hg [58]. Similarly, the autonomic nervous system (ANS) was also found to be affected strongly by Hg exposure. Fatigue, powerful sweating, abdominal pain, and hypertonia of the artery are some of the signs found in children exposed to Hg; indicating the presence of mercury effects on the ANS [59].

High blood pressure and fatal heart attack have been observed in people exposed to Hg [60, 61]. Research findings have shown a correlation between prenatal exposure to Hg and impaired neurological development in children [62]. All these studies demonstrated the toxic effects of Hg on the human cardiovascular system. Furthemore, human exposure to Hg has been reported to lead to various skin diseases, anxiety disorders, and contact dermatitis [63, 64]. Majorly, acrodynia arises from exposure of the skin to mercurous chloride (Hg_2Cl_2) utilized in teething powder or diaper laundering due to its antibacterial properties [65].

Some studies have also claimed that exposure to Hg could cause several kidney diseases. For instance, Hg in its elemental and inorganic forms is highly harmful to the renal

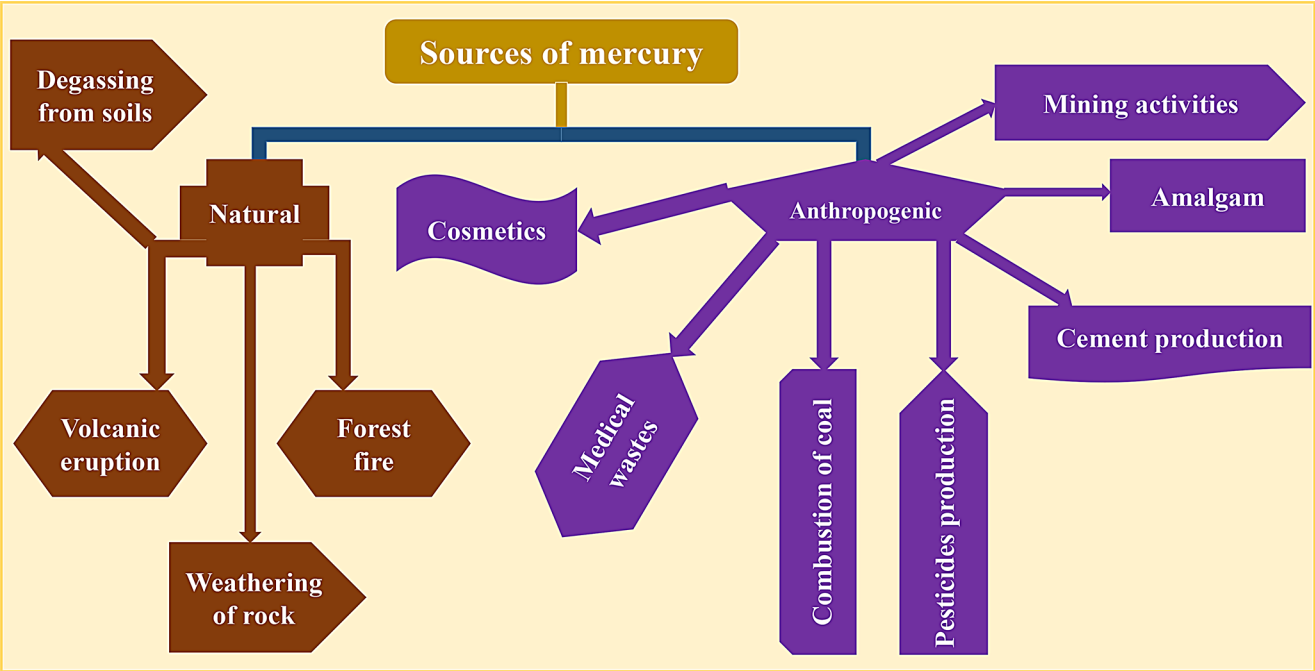

Fig. 3 Main sources of mercury in the environment

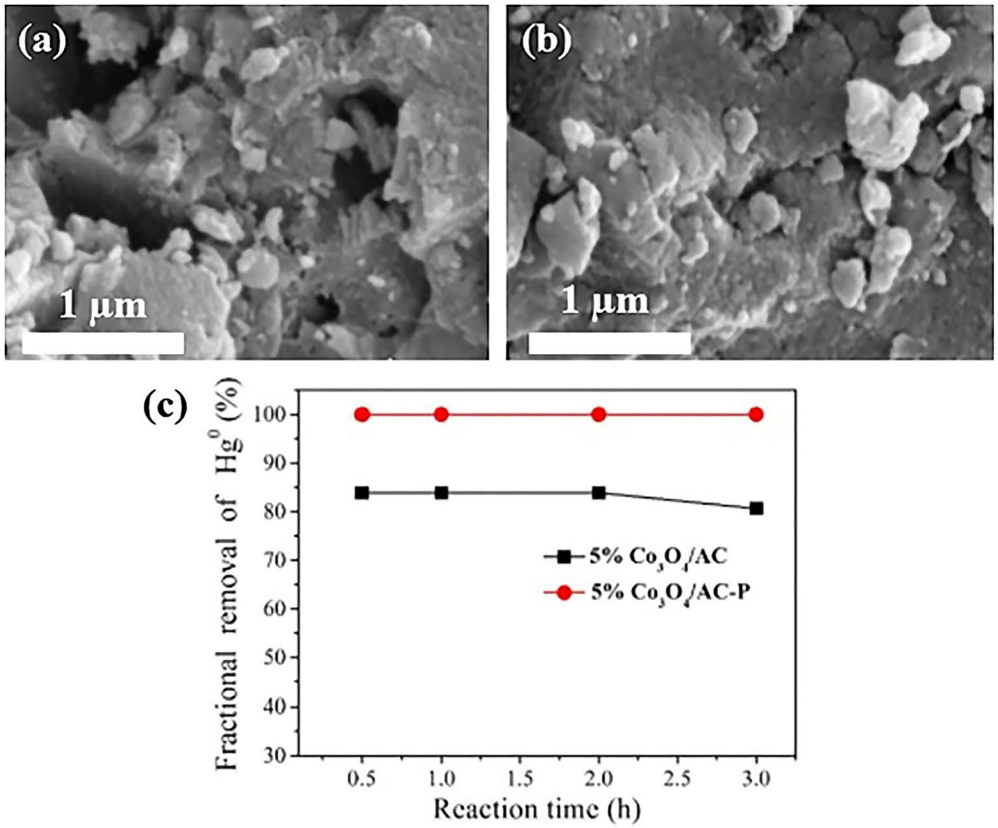

Fig. 4 SEM images of (**a**) 5% Co_3O_4/AC, (**b**) 5% Co_3O_4/AC-P (P indicates preparation by plasma heating). (**c**) Mercury removal efficiency. Data are obtained from [82]

Table 1 Properties of different forms of mercury and its sources

Mercury Sample	Molecular formula	Oxidation state	pH	Sources	Reference
Elemental mercury	Hg	0	-	Flue gas	[42]
Mercury solution	$Hg(NO_3)_2$	+2	3.0–7.0	solution	[43]
Mercury solution	$Hg(NO_3)_2$	+2	2.0–6.0	solution	[44]
Mercury chloride	$HgCl_2$	+2	2.0–8.0	solution	[45]
Mercury nitrate	$Hg(NO_3)_2$	+2	2.0–10	solution	[46]
Mercury cyanide	$Hg(CN)_2$	+2	3.0–11	wastewater	[47]
Mercury chloride	$HgCl_2$	+2	2.0–8.0	wastewater	[48]
Mercury chloride	$HgCl_2$	+2	3.0–7.0	wastewater	[49]
Mercury nitrate	$Hg(NO_3)_2$	+2	3.0–9.0	solution	[50]
Mercury chloride	$HgCl_2$	+2	5.0–12	solution	[51]

system and tissues [65]. In this case, owing to the accumulation of Hg deposits in renal tissues, some enzymes were released into urine. Such occurrence is frequently seen as an indicator of renal system damage. Additionally, intracellular enzymes like lactate dehydrogenase, aspartate aminotransferase, and acid phosphatase were reported to have found their way into the urine of some individuals besides proteins like albumin at high levels of exposure [66, 67]. Glomerulonephritis (malfunction of the renal system) was observed in industrial-exposed human residents and animal studies [65]. All these studies clearly showed that Hg is a harbinger of death, and hence, sustainable techniques should be developed for its management.

Following the identification of both the sources and toxicity of mercury, the subsequent section illuminates various methodologies employed to synthesize metal oxide adsorbents aimed at mitigate mercury contamination in the environment.

2 Strategies for the Preparation of Metal Oxide-Based Adsorbents

Metal oxide-based catalysts are being adopted for the removal of mercury (Hg) due to their effectiveness in Hg oxidation, low toxicity, and sulfur resistance. This is because of the availability of variable oxidation states and rich surface oxygen [72–74]. Metal-based oxide catalysts are attracting research interest for the adsorbing of Hg and other harmful heavy metals due to their good chemical stability, low cost, and higher number of active sites [71]. By and large, metal oxide-based adsorbents can be categorized into metal oxide-supported adsorbents and non-supported adsorbents. The use of support enhances the specific surface area of the metal oxide catalysts, which are usually carbon materials or other metal oxides in composites [69, 72, 73]. The application of a magnetic field in removing mercury pollutants is also an appealing proposition for using magnetic metal oxide adsorbents [71].

Concerning the metal oxide characteristics, different synthetic procedures have been adopted to optimize and improve their removal efficiency towards Hg [74]. Up to this moment, different methods of syntheses ranging from hydrothermal, impregnation, plasma, sol-gel, microwave, and deposition-precipitation, to co-precipitation methods have been employed for the synthesis of metal-based adsorbents.

2.1 The Impregnation Method

Impregnation is among the extensively used method of preparation for heterogeneous catalysts, because of its sustainable nature, affordability, and direct implementation procedure. This is categorized into two, specifically (1) Wet impregnation and (2) Incipient wetness impregnation. In the wet impregnation method, a surplus amount of solution is absorbed into the support while an appropriate amount of solution is loaded into the support pore volume [75]. In both methods, the support is impregnated with a precursor solution, dried, and calcinated to form the intended catalyst.

For instance, MoO_3/CeO_2-activated carbon ($MoO_3/CeO_2/AC$) is synthesized by the incipient wetness impregnation method, where a measured amount of precursor solution is filled into the AC pores. When applied for mercury adsorption, the sample with a higher specific surface area adsorbed mercury most. This, in turn, demonstrates the best stability with higher resistance to water vapour [76]. Similarly [70], prepared CuMnOx-supported Al_2O_3 (CuMnOx/Al_2O_3) by incipient wetness impregnation method, where the impregnated precursor solution contains 20% wt each of CuO and MnO. It has been confirmed that bimetallic metal oxide adsorbents exhibit superior mercury oxidation compared to single metal oxides, due to synergistic effects between the two metal oxides. Also, the Hg adsorption by CuMnOx/ Al_2O_3 is further confirmed from morphological and structural characterization, where noticeable changes are observed in the morphology and crystallite structure of the adsorbent after the adsorption process.

In another way, a bimetallic La_2O_3/Bi_2O_3 catalyst in the form of a composite is synthesized by the wetness impregnation method. In this method, an appropriate amount of La precursor is impregnated into Bi_2O_3, dried, and calcinated at different temperatures. A noticeable difference in phase structure and morphology is also observed on varying the calcination temperature, which influences their adsorption capacity. A catalyst with the highest average pore diameter at 6% wt La_2O_3 is considered for optimal adsorption. Thus, the adsorption capacity of the La_2O_3/Bi_2O_3 catalyst is believed to be influenced by the sample composition, morphology, electronic structure, and calcination temperature [74]. Similarly, V_2O_5-WO_3 (1: 8% wt) composite is synthesized on TiO_2 support by the wet impregnation method. First, a precursor solution of Vanadium and tungsten is formed and then impregnated into the pores of commercial TiO_2 support to obtain the needed V_2O_5-WO_3/TiO_2 adsorbent. When applied for mercury adsorption, it is discovered that longer reaction time and higher CO_2 concentration favours higher adsorption capacity of V_2O_5-WO_3/TiO_2 adsorbent [77].

2.2 The Co-Precipitation Method

This is a specialized method that requires the use of complex instruments for effective control of conditions needed for hetero-catalyst adsorbents. It is believed to be appealing for commercial production of metal oxide catalysts because of its capacity to achieve a higher metal loading with a smaller particle size. It is considered the best way to prepare metal oxide catalysts of high metal weight-to-volume ratio, while a large volume of water is required to separate the product from massive salt solutions. However, local fluctuations do occur due to poor mixing or temperature gradient leading to non-uniform growth patterns. The co-precipitation method comprises three important steps precursor reaction, nucleation, and crystallization process [75, 78].

In a bid to synthesize metal oxide catalysts with excellent adsorption capacity for Hg, a metal oxide composite is prepared from layered double hydroxide (LDH) by the co-precipitation method. Mesoporous Mn/CoAlOx catalyst [79] is prepared by the co-precipitation under the constant supply of N_2 followed by the calcination process. As-prepared Mn/CoAlOx catalyst displays a regular flower-like morphology with a large surface area, a characteristic suited for adsorption. When tested, it exhibits a magnificent.

Hg oxidation with resistance to water and sulfur poisoning. It is concluded that the Mn introduction enhances the adsorption capacity of Mn/CoAlOx through the increase of surface active sites.

By utilizing the large surface area offered by the substrate, oxides of manganese and cerium are synthesized on Al_2O_3 ($Mn_xCe_{0.3-x}Al$) support by the co-precipitation method. When applied for Hg adsorption it exhibits excellent adsorption capacity with a removal efficiency of about 96% at optimum calcination temperature. By applying different calcination temperatures it is discovered to have varying effects on the Hg removal efficiency. A synergy between MnO_2 and CeO_x is also believed to enhance the activity of $Mn_xCe_{0.3-x}Al$ towards Hg adsorption [80].

2.3 The Plasma Method

This involves the use of Plasma heating for the preparation of different types of metal oxides by varying means of external heating sources. This method of preparation is rapid and effective due to the direct heating of the samples by plasma [81]. For instance, Yu and coworkers synthesized cobalt oxide on activated carbon (Co_3O_4/AC-P) by plasma heating and compared it with the one prepared by the wetness impregnation method. Results from morphological and surface functional group characterizations indicate no visible changes in the functional group and structure at the surface (Fig. 5). When Co_3O_4/AC-P catalyst is applied for mercury adsorption at a temperature above 120 ºC, it demonstrates removal efficiency of about 100%. The excellent activity is due to a high number of surface active sites by plasma heating [82] Fig. 4.

Similarly, Sobhanardakani and co-researchers [46] prepared Fe_3O_4 thin film on SiO_2 (Fe_3O_4/ SiO_2) substrate by plasma-induced chemical vapour deposition. The adsorption capacity of Fe_3O_4/ SiO_2 thin-film for Hg^{2+} is believed to improve by increasing the pH above 6.0. This is possible through the interaction of Hg^{2+} and the deprotonated ions caused by increased pH conditions.

2.4 The Hydrothermal Method

This method describes the synthesis process for preparing metal oxides at higher temperatures in aqueous solutions. The synthesis is usually carried out at a pressure above atmospheric one in a sealed stainless steel autoclave. This method can also synthesize high-quality crystalline materials, though not as highly crystalline as those being prepared

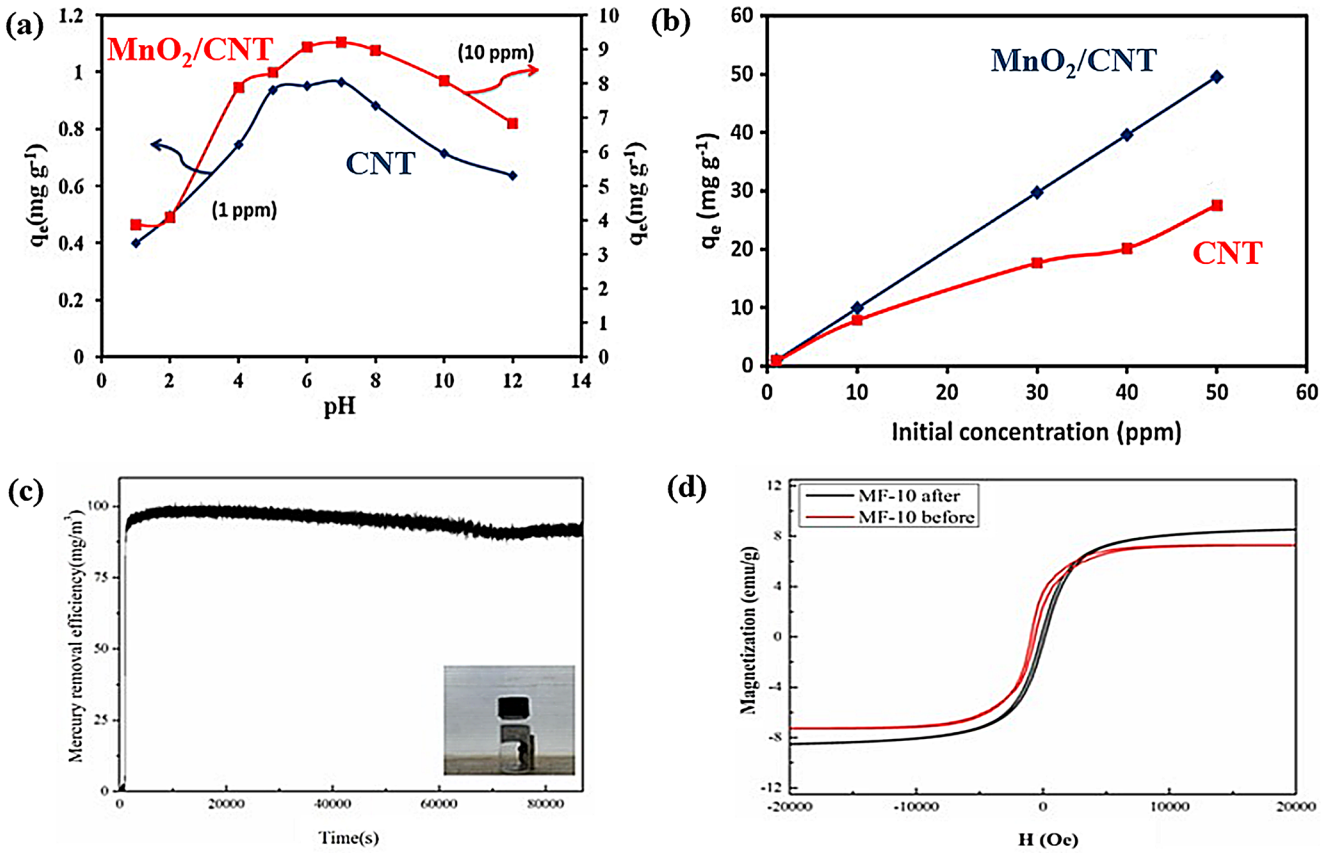

Fig. 5 (**a**) Effect of pH on the adsorption of Hg^{2+}. (**b**) Effects of initial concentration on the Hg^{2+} adsorption. Data are obtained from [84]. (**c**) Mercury removal efficiency over 24 h. (**d**) cyclic experiment before and after adsorption. Data are obtained from [85]

by the co-precipitation method. It is easy to set up at a relatively low cost and produces a high yield of products [83].

For example, manganese oxide is prepared on carbon nanotube (MnO_2/CNT) by hydrothermal method at a high temperature of 160 ºC. The product is later washed with distilled water and dried in an electric oven. The adsorption capacity of MnO_2/CNT composite (110.38 m^{-2} g^{-1}) is far greater than ordinary carbon nanotube (91.27 m^{-2} g^{-1}) at varying pH and concentration conditions, due to larger specific surface area (Fig. 5; [84]. By using the high number of surface active sites presented by composites [85], synthesized MoS_2/Fe_3O_4 catalyst by a two-step hydrothermal reaction. This is achieved by systematically altering the quantity of Fe_3O_4 within the composite, subsequently employing it for mercury adsorption. Maximum adsorption removal of about 100% is obtained with 10 wt% Fe_3O_4. It is considered a good adsorbent because of its high efficiency and ease of recycling. More so, it displays excellent stability over 24 h (Fig. 5).

2.5 The Sol-gel Method

This is another method of producing metal oxide catalysts enabling effective control of reaction conditions. The principle of the sol-gel method is established on hydrolysis and polycondensation reactions. With a sol-gel method of preparation, it is feasible to obtain materials of greater surface area and stable surface [86].

Through the sol-gel method, iron oxide-alumina (Fe_2O_3/Al_2O_3) nanocomposite fibers are synthesized after heating at a higher temperature of about 1000 ºC. When applied for adsorption procedures, Fe_2O_3/Al_2O_3 nanocomposites display an optimum removal efficiency of about 90%. The excellent performance of the Fe_2O_3/Al_2O_3 nanocomposite is traced to its rough and fibrous morphology, leading to a higher number of surface active sites [87]. Similarly [88], synthesized $LaFeO_3$ perovskites and investigated their adsorption efficiencies to other metal oxides. When applied for the oxidation of elemental mercury under different reaction temperatures, $LaFeO_3$ nanoparticles exhibit a removal efficiency removal of about 94% at 120 °C. The performance could be attributed to the unique structure of perovskite that enables change in the Fe valence state, leading to the release of lattice oxygen. The comparative performance with other metal oxides and temperature is shown in Fig. 6. In studies carried out on metal oxides so far, appreciable removal efficiencies have been recorded under moderate reaction conditions (Table 2).

3 Factors Affecting the Adsorption of Mercury from the Solution

Several parameters are crucial in determining the quantity and the rate at which mercury is adsorbed from the aqueous medium. These parameters are adjustable to attain optimized adsorption performance. The parameters include pH, initial concentration, contact time, adsorbent dosage, and temperature, which shall be discussed in the section below.

3.1 Effect of pH

The pH of the solution significantly impacts the adsorption of Hg by affecting the interaction between the surface charges of the adsorbents and the functional groups of the mercury. For instance, Sun and co-workers compare the adsorption capacity of Iron sulfide (FeS) and pyrite for mercury across a pH range of 3 and 11, demonstrating the

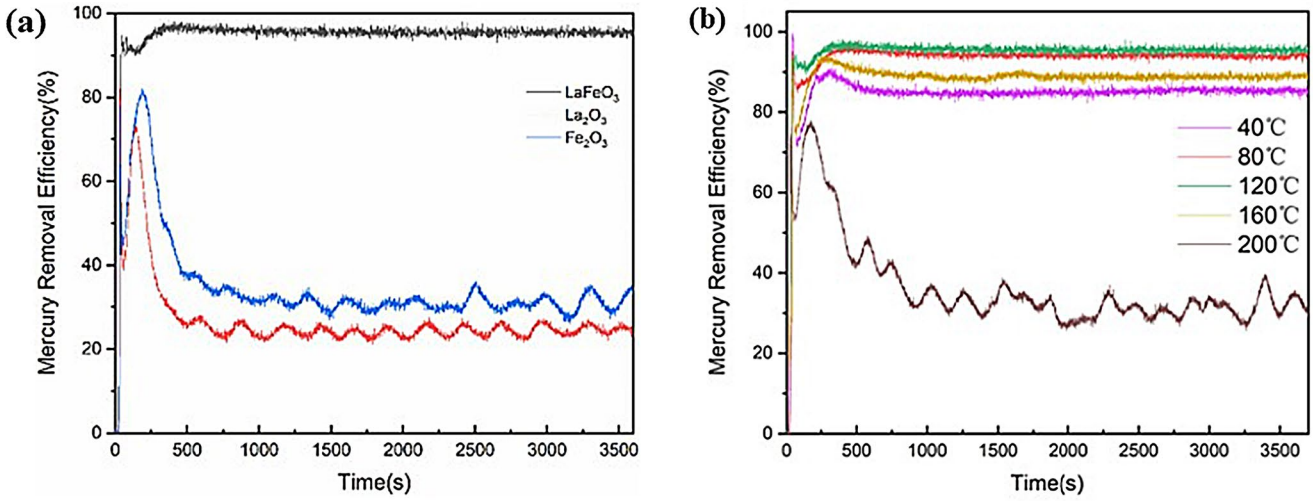

Fig. 6 (**a**) Effect of $LaFeO_3$, La_2O_3, and Fe_2O_3 on the removal efficiency of Hg^0. (**b**) Effect of temperature on the adsorption of Hg^0. Data are obtained from [88]

Table 2 Metal oxide samples, synthetic method, and their reaction performance

Sample	Synthesis method	Removal efficiency %	Reaction temperature °C	Time min	Reference
Mn/MgO	Impregnation	82	120	-	[89]
Se@ZnO-NR	Wet chemical method	≥99.2	=	60	[90]
d-MoS_2/Fe_3O_4	Hydrothermal	>99	50	30	[91]
$LaFeO_3$	Sol-gel	~94	120	30	[88]
Co_3O_4/AC	Plasma	~100	150	180	[82]
MnO_x-SnO_2	Co- precipitation	95	150	210	[92]
Cys-Fe_3O_4	Precipitation	95	25	20	[93]
Fe_3O_4/rGO	Solvothermal	86.72	37.3	50	[94]
Au-Al_2O_3	Precipitation	>97	25	30	[95]
TiO_2 NT	Hydrothermal	96	25	20	[96]

critical role of pH in optimizing adsorption. When applied for the treatment of mercury in acidic conditions (pH 3), almost 99% removal efficiency is observed on FeS while 28% removal is displayed by pyrite. This is attributed to the interaction between sulfur-containing groups released during dissolution and Hg^{2+} of the FeS. At a pH of 9, the removal efficiency of mercury on FeS also supersedes pyrite due to easy adsorption of hydroxide mercury sediment produced [97]. In another study by Bandaru and co-researchers, thiol-derivatized single-walled carbon nanotubes (SWCNT-SH) were utilized for the remediation of mercury within the pH range of 1 to 9. A consistent removal is observed as the pH increases from acidic conditions, achieving a removal efficiency of 98% at a pH of 9. However, the removal efficiency decreases when the pH drops below 4, attributed to adverse interaction between the competing species [98].

3.2 Effect of Initial Concentration

The initial concentration of the adsorbate has a significant impact on the adsorption capacity of the adsorbents, and this relationship can be either positive or negative depending on a variety of factors such as electrostatic repulsive interactions, saturation of adsorption sites, and steric hindrance. Generally, most studies on mercury adsorption found a positive connection between ion uptake and initial concentration adsorption from aqueous solutions [99]. For example, Sheela and co-workers studied the effects of the initial concentration of Hg ions on the adsorption capacity of ZnO and demonstrated their positive dependence on the initial concentration. Because of the higher driving force induced by the concentration gradient, equilibrium adsorption increases as the initial concentration of Hg ions increases. This tendency continues until a climax is achieved, at which point the adsorption capacity ceases to rise due to the complete usage of the adsorbent's surface active sites [100]. In a study conducted by Wang and colleagues, iron oxide-coated silicon modified with thiol (Fe_3O_4@SiO_2-SH) was synthesized for Hg^{2+} adsorption. Upon application, the results reveal a positive correlation between the initial concentration and adsorption capacity. However, an intriguing observation is made as the initial concentration increases, leading to a decrease in removal efficiency. This significant finding, reported by [101], underscores the complexity of the adsorption process and prompts further exploration into the underlying mechanisms governing the interaction between the adsorbent and the adsorbate (Hg^{2+}).

3.3 Effect of Contact time

Contact time stands out as a pivotal parameter influencing adsorption capacity, representing the time required for the adsorption process to achieve equilibrium. This process is contingent upon certain factors such as the abundance of surface active sites, the pore size characteristics of the adsorbents, and the concentration gradients of mercury ions in the solution [45]. In line with the above statement, a study conducted by Khorshidi and colleagues investigated the adsorption behavior of a nickel ferrite graphene oxide composite ($NiFe_2O_4$/GO). Notably, their findings showed substantial and rapid adsorption within the initial 60 min of the reaction time, followed by a decrease in adsorption toward 90 min, signifying the attainment of equilibrium [102]. This observation aligns with the common trend where adsorption proceeds rapidly in the initial stages, attributed to the abundance of surface active sites until a state of equilibrium is reached.

3.4 Effect of Adsorbent Usage

Studies have revealed a notable correlation between adsorbent dosage and the dynamics of adsorption capacities and removal efficiencies [103]. In a related study, Mahmoud and co-workers synthesized activated carbon nanoparticles, integrating thiol and Fe_3O_4 modifications. The application of this prepared sample for mercury removal exhibits commendable removal efficiencies. Notably, an upward variation in adsorbent dosage correlated positively with an enhancement in the removal efficiency of mercury. This

observed performance is attributed to the increased surface activity resulting from the incorporation of the thiol group.

However, it is imperative to acknowledge that prolonged removal of Hg ions, while initially bolstering removal efficiency, eventually diminishes the number of available active sites. This phenomenon, in turn, contributes to a reduction in adsorption capacity, highlighting the complicated balance between adsorbent dosage and sustained efficacy over extended periods [104].

3.5 Effect of Temperature

Several researchers have demonstrated the dependence of temperature on the adsorption capacity. In a study conducted by Das and co-researchers, MnO_2 was applied for the removal of mercury from solution at different temperature ranges. The observed pattern clarifies a temperature-dependent phenomenon in which mercury absorption shows a progressive trend with rising temperatures, reaching its maximum adsorption capacity at a crucial temperature point, and after that showing a noticeable decrease [105, 106]. This effect could be attributed to the weak interaction that exists between the targeted mercury ions and the active sites of the carefully produced MnO2 adsorbent. As the temperature increases the tendency for more interaction speeds up, which ultimately leads to an ideal adsorption state. The above pattern is also observed when the as-prepared CuO composites prepared by Al-Hazmi and co-workers are applied for the removal of Hg from the aqueous solution until an optimum is reached. The reduced binding affinity between the active sites of the as-prepared adsorbent and the mercury ions causes the adsorption's effectiveness to decrease after this point [105, 107].

3.6 Mechanism of Adsorption of Mercury Ions in Aqueous Media

Mercury ions in solution can interact via physical adsorption, facilitated by weak van der Waals forces, and electrostatic interactions with the surface of the adsorbent which is more prominent when the pH of the aqueous medium is greater than the point of zero charge of the adsorbent. This interaction is enhanced by the high surface area and porous nature of the adsorbent [108, 109]. Mercury ions located at the surface of the adsorbent can subsequently engage with suitable reactive sites present on the adsorbent's surface [108]. The hydroxyl group has been identified as a significant functional group that is present in metal oxide adsorbents or surrounding metal oxide-based adsorbents during an adsorption process, particularly at higher pH levels as variation occurs [110]. Mercury ions in solution can coordinate with the oxygen atoms of the hydroxyl functional group at the surface of the metal oxide-based adsorbent to form a stable complex, leading to the immobilization of mercury on the metal oxide surface [109]. While both surface area and functional groups contribute to the adsorptive removal of mercuric ions from aqueous media, the combination of medium to high surface area with well-functionalized surface properties is collectively crucial in enhancing the adsorptive removal of mercury ions, through both physical adsorption and chemical adsorption mechanisms, from aqueous media [111].

3.7 Regeneration of Metal Oxide-Based Adsorbents

For both economic and environmental sustainability, disposing of adsorbents as waste after a single use is considered imprudent [112]. Instead, efforts are focused on developing sustainable and cost-effective methods for the regeneration and reuse of adsorbents, aligning with environmentally conscious practices and resource optimization. Thermal and chemical regenerations are two frequently employed methods for the recovery of metal oxide-based adsorbents from sorbed mercury.

Thermal regeneration involves subjecting the spent adsorbent to elevated temperatures in an inert environment, effectively driving off adsorbed pollutants and restoring the material's adsorption capacity for subsequent use [113]. Chemical regeneration emerges as an advantageous alternative when adsorbents lack thermal stability. This chemical regeneration method entails utilizing specific and suitable solutions to desorb pollutants from metal oxide-based adsorbents, rejuvenating their adsorption capabilities [114]. Adsorbed ions of Hg (II) distributed in the surface region of Fe_3O_4-based adsorbent were removed by treating them with the chelate reagent EDTA [115].

Metal oxides have been demonstrated to display excellent removal efficiencies for mercury treatment, due to their high surface area, porosity, and the presence of a high number of surface active sites. However, metal oxides tend to aggregate over time, leading to a decrease in their adsorption efficiency.

4 Conclusion and Future Perspectives

These regeneration techniques help extend the lifespan of the adsorbent and reduce economic and environmental footprints associated with frequent disposal. The choice between thermal and chemical regeneration depends on the nature of the adsorbent and the targeted pollutants, emphasizing the importance of tailored approaches for optimal sustainability outcomes.

This review provides a brief and detailed overview of the efforts for the removal of mercury in the environment via the use of readily available earth-abundant metal oxide adsorbents, covering the methods of their preparations, contributing factors affecting their adsorption performance, regeneration capabilities, and challenges in future applications. With increasing access to cheap earth-abundant metal oxides, removing mercury from the environmental media and its harmful effects on humans is achievable and highly feasible.

As we move forward, the accessibility of cost-effective earth-abundant metal oxides offers a viable path toward achieving practical and efficient mercury removal from environmental sources, hence reducing possible negative health impacts. The insights garnered from this review underscore the significance of ongoing research and development in improving adsorption performance and addressing regeneration issues. Here are some more suggestions that could be made:

- Innovation in synthesis techniques for metal oxide adsorbents should be a priority, focusing on sustainable synthesis/nanoscale engineering that may produce materials with enhanced adsorption capabilities.
- Gaining more insight into the fundamental mechanisms that control the adsorption process is crucial. Investigating the interactions between metal oxide characteristics, environmental conditions, and mercury species will contribute to the development of more efficient and selective adsorbents.
- Thorough evaluations of the environmental impact of metal oxide adsorbents are essential as their use rises. This includes evaluating any potential leaching of contaminants from the adsorbents and ensuring the overall sustainability of the technology.
- It is necessary to carry out the metal oxide regeneration to increase economic feasibility. Unfortunately, regeneration is neglected in the adsorption processes.

By implementing the above recommendations, we can advance the study towards a more resilient and environmentally responsive approach, safeguarding ecosystems and human health from the prevalent threats posed by mercury contamination.

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Declarations

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