

EFFECT OF ALUMINA AND THIOL'S ROLES FOR Hg^{2+} ADSORPTION IN WASTEWATER – A SHORT REVIEW

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Abstract. The issue of mercury (Hg^{2+}) existing in water supplies has been brought up since it has an impact on both people and the environment. The ideal method for removing Hg^{2+} is adsorption since it is easy to use, highly effective, and economical. Alumina composite and thiols are two probable substances that have been used to remove Hg^{2+} from wastewater, but it is still unclear how these substances work when it comes to adsorbing the metal. In order to observe the present method of removing Hg^{2+} from wastewater, this review has been undertaken. This study examined the characteristics, processes, and qualities of two different types of adsorbents: alumina and thiol. There are numerous phases of alumina, and each has distinct properties. The characteristics of alumina at various temperatures, levels of porosity, and surface area, as well as its primary identification as a Hg^{2+} adsorbent by the bonding of Al-Hg in XPS, XRD, and TEM, are described. Additionally, through imaging and bonding confirmation of S-Hg utilising FE-SEM, FTIR, and XPS, the function of thiol as a soft base and the major characterization as a Hg^{2+} adsorbent is demonstrated. This study shows that alumina's gamma phase is widely employed as a composite material while thiol, with its functional group, -SH, is the most efficient substance for capturing Hg^{2+} . Due to the characteristics of each, alumina and thiol have the ability to bond with Hg^{2+} . For future reference, this review paper emphasises the importance of alumina and thiol as adsorbents for Hg^{2+} removal.

Keywords: Alumina, thiol, adsorption, adsorbent, mercury

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Introduction

Apart from solid waste pollution, mercury contamination in water resources has recently become a significant problem due to the widespread of mining, electroplating, smelting and other industries [1]. Mercury can be found in air and soil, aside from water [2]. The common mercury species that can be found accumulated in water is Hg^{2+} [3]. Global attention has been drawn to mercury issues because they pose concerns to human health and other living things through bioaccumulation in the food chain, such as when people eat seafood that contains mercury. The mercury exposure can lead to chronic poisoning after it being accumulated in certain organs of our body through ingestion. We can infer from bioaccumulation that aquatic life is also at risk from Hg^{2+} exposure in addition to humans. Before it gets out of our hands, we as intelligent humans should take care of this issue.

To remove Hg^{2+} as fully as feasible, researchers have developed a variety of techniques, including reverse osmosis, nanofiltration, ion exchange, coagulation, membrane filtration, co-precipitation, and adsorption. Due to its straightforward methodology, high efficiency and low-cost technologies, adsorption is one of the most widely used methods to address the problem. In order to establish more effective, environmentally friendly, and affordable production and operational costs, researchers have produced novel adsorbents over a long period of time using previous studies as references. According to numerous studies, a good adsorbent should have a large surface area with active binding sites, a high hydrothermal stability, a great affinity for the target, and the capacity to endure severe environments [4]. To develop a good adsorbent, such qualities should be taken into account.

According to earlier studies, the optimal pH for mercury adsorption is 5.5. The study suggests that Hg(II) exists in aqueous solution in three possible states: Hg^{2+} , Hg(OH)^+ , and Hg(OH)_2 . Hg(OH)^+ will be at its highest concentration around pH 4, whereas Hg(OH)_2 will be dominating at pH levels more than 6. Both species will be adsorbed by thiol equally without electrostatic repulsion (which occurs when Hg^{2+} adsorption peaks during thiol group formation and Hg^{2+} forms a complex) [3]. Mercury adsorbents can be created from a number of different sources. Table 1 lists the adsorbents that have been synthesised and applied in prior investigations. Adsorption effectiveness might be impacted by contact time as well. Equations 1 and 2 were used to calculate the adsorption efficiency (AE) (%) and amount (mg) of mercury ions (Hg^{2+}) adsorbed onto the composite adsorbent (g):

$$\text{AE}\% = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

$$q = \frac{(C_i - C_e)}{m} \times V \quad (2)$$

where C_i = initial mercury concentration, mg L^{-1}

C_e = equilibrium concentration of mercury in solution, mg L^{-1}

Q = amount of mercury adsorbed per unit mas of adsorbent, mg g^{-1}

V = volume of mercury solution, L

m = mass of composite adsorbent, g

Table 1: Summary of adsorbents of mercury

Adsorbent	Adsorption Efficiencies (%)	References
Polymer modified activated carbon (AC/DETA-TMC)	95% after 40 minutes.	[2]
Cysteamine modified partially reduced graphene oxide (Cyst-prGO)	96 % removal of mercury in 10 minutes with 10 mg L ⁻¹ dose of Cyst-prGO.	[5]
[SnS ₄] ⁴⁻ /MgFe-LDH composites *layered double hydroxide (LDH)	99.9% with lower than 25 mg/L of C _i after 1 hour.	[6]
two-dimensional MXene	99.9% with 100 mg/L of C _i after 24 hours.	[7]

Adsorption affinity is often higher than 94 % for the majority of the reported adsorbents. Polymer modified with activated carbon exhibits the lowest adsorption affinity of 95 %. The adsorbents differ in terms of contact time as well, with AC/DETA-TMC having the shortest contact time (40 minutes).

In earlier studies, the removal of heavy metal ions including Hg²⁺ from wastewater was frequently discussed using the adsorption approach. One of the study is how it mentioned various conventional methods (electro dialysis, chemical precipitation, coagulation/flocculation, ultrafiltration, adsorption and reverse osmosis) available to remove heavy metal. According to the article, adsorption is more frequently utilised than other techniques because of its simple operation and low cost. Although other adsorbents, such as alkalized alumina, were addressed, the attention was mainly on natural or modified bentonite [8].

According to the second review, the removal of pollutants from groundwater necessitates the use of adsorption as one of the tertiary, or last, water treatment methods, along with reverse osmosis, precipitation, ion exchange, and oxidation. The ability of adsorption to remove both soluble and insoluble contaminants from wastewater makes it the most effective universal approach, claims the study. The study also included a brief description of physisorption and chemisorption as well as a broad overview of the adsorption process. Along with other adsorbents (such as chitosan, activated carbon, zeolites, silica gel, and clay), activated alumina was listed as being used to treat wastewater. In the paper's discussion of nano adsorbents, alumina was also used to remove biological and organic contaminants as well as inorganic pollutants like lead (Pb), cadmium (Cd), chromium (Cr), and mercury (Hg²⁺) [9].

The most well-liked and effective method to remove contaminants, particularly heavy metals in wastewater (mainly Hg²⁺) has been emphasised in various review publications [8,9]. Although alumina was frequently cited in those studies, neither an explanation of which phase it was in nor an example of Hg²⁺ adsorption onto alumina were provided. Thiol is also frequently cited in studies due to its functional group -SH, which is so compatible with Hg²⁺. Despite this, there has been limited progress in characterising the interaction between thiol and Hg²⁺. Just XPS was used to characterise the interaction between thiol and Hg²⁺; FTIR, TEM, and FE-SEM were not thoroughly discussed. This review is therefore done to close the gap left by the other reviews.

Alumina as Adsorbent

When treated with sufficient thermal treatment, alumina, whose main source is bauxite ore, has multiple phases that are classified as α (most stable phase), γ , η , θ , χ , δ and κ [10]. The γ -alumina had been a particularly important topic among researchers since it has potential in adsorption and as catalyst support [11] as it has high thermal stability, specific surface area, has porous technology for better dispersion catalyst species, high chemical stability and has low toxicity and also can be used for water treatment. Many processes, including sol-gel synthesis, precipitation, laser ablation, spray pyrolysis, hydrothermal/solvothermal, biomimetic and a plasma jet mixed with a vapor phase precursor [10], can be used to create γ -alumina. The terms α and γ are frequently used and discussed in mercury adsorption. As shown in Table 2, both phases have unique characteristics that influence their responsibilities in piquing researchers' interest in water treatment research.

Table 2: Phase of γ and α alumina and their characteristics

Phase of alumina	Characteristics	Reference
γ	- has high specific surface area.	[10]
	- high purity (low toxicity).	[10]
	- has excellent dispersion.	[10]
	- resist to high temperature.	[10]
	- high catalytic activity.	[10]
α	- has low specific surface area.	[11]
	- resist to high temperature.	[11]
	- almost has no catalytic activity.	[11]

The features of the phase emphasised by the γ phase in Table 2 have demonstrated that the phase is preferred as a catalyst support and adsorbent, particularly its characteristic that has catalytic activity exhibited more obviously than the α phase. Hence, it has been established that the γ -phase is the best phase for aiding in the treatment of water.

Figure 1 depicts the mechanisms of Hg^{2+} ion adsorption over γ -alumina surface sites. On γ -alumina, HgCl_2 forms chemical bonds. Lewis Al^{n+} -Bronsted O^{n-} pairs, hydroxyl (Al-OH) and the coordinatively unsaturated oxygen (O_2^- ions) provide effective basic sites for the chemisorption of HgCl_2 on γ -alumina [12].

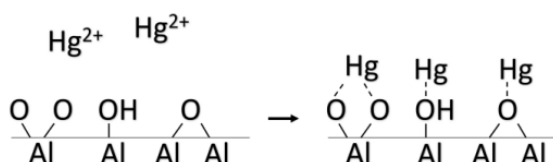


Figure 1: Schematic diagram of alumina adsorbing HgCl_2

Examples of alumina and alumina composites used in mercury adsorption are shown in Table 3. Aluminum cans can be used to make alumina. Energy can be saved by using those materials in place of commercial alumina. Magnesium, iron, and manganese are impurities in aluminium cans, which contain almost entirely aluminium as its main component [13].

Table 3: Alumina and alumina composite for Hg^{2+} adsorption

Product	Outcome	Reference
Biomimetic self-curved nanoplates assembled coral-like nanoporous $\gamma\text{-Al}_2\text{O}_3$.	49.15 mg/g of $\text{Hg}(\text{II})$ removal capacities	[14]
$\text{Pd/Ce}/\gamma\text{-Al}_2\text{O}_3$	98% of AE within 480 min at 250 °C and 91% of AE within 200 min at 300 °C	[15]
Iron oxide-alumina mixed nanocomposite fiber.	63.69 mg/g of Hg^{2+} maximum sorption capacities.	[16]

When pore volume and specific surface area of γ -alumina rise, so does the percentage of Hg^{2+} adsorption efficiency. Time spent soaking and calcination temperature have an impact on the volume of pores and the specific surface area of γ -alumina. Phase composition, diameter, and surface area can all be impacted by temperature during calcination [17]. Hand grinding can produce fine γ -alumina powder. Although material characteristics may alter if lowered to the nanoscale, this is done to generate fine-powdered nanoparticles [18]. High surface area with high pore volume, in addition to mesopores with a size range of 2 to 50 nm, are required to produce mesoporous alumina of good quality [19].

Characterisation of Alumina and Alumina Composites for Hg^{2+} Adsorption

This section described three primary methods, namely X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD), and Transmission Electron Microscopy (TEM), for characterising alumina and alumina composites for Hg^{2+} adsorption.

X-ray Photoelectron Spectroscopy (XPS)

The elemental composition and electronic state of the atoms in the adsorbent are compared before and after the procedure using XPS. Coral-like γ -alumina was utilised as the Hg^{2+} adsorption medium in one of the earlier investigations that employed XPS. In contrast to the spectra taken before adsorption, the peak $\text{Hg}4f$ at 102 eV was present in the spectra, showing that Hg^{2+} was present in the sorbent after the adsorption process. Once adsorption demonstrated the existence of the Hg-O component, detailed spectra for $\text{O}1s$ at 529.9 eV were discovered. After the adsorption, signals with binding energies of 531.5 eV (assigned for Al-O groups) and 532.6 eV (assigned for $-\text{OH}$ groups) shifted marginally to higher binding energy positions [14]. Research [20] further demonstrated that the removal of mercury was possible using molybdenum disulfide-enabled alumina ($\text{MoS}_2@\text{Al}_2\text{O}_3$), which was produced at 180 °C. According to the study, redox reactions are the active removal processes, and when the removal procedure was carried out, new peaks appeared. The peaks appeared to be the byproducts of redox reactions, such as the oxidation of S^{2-} to SO_4^{2-} (S^{+6}) and MoO_2 (Mo^{+4}) to MoO_3 (Mo^{+6}). In contrast, $\text{MoS}_2@\text{Al}_2\text{O}_3$ synthesised at 210 °C exhibits no appreciable peak alterations following the removal procedure. When $\text{MoS}_2@\text{Al}_2\text{O}_3$ is synthesised at 210 °C, MoS_2 oxidation is not the predominant route of removal. The explanation of research [20] is according to Figure 2.

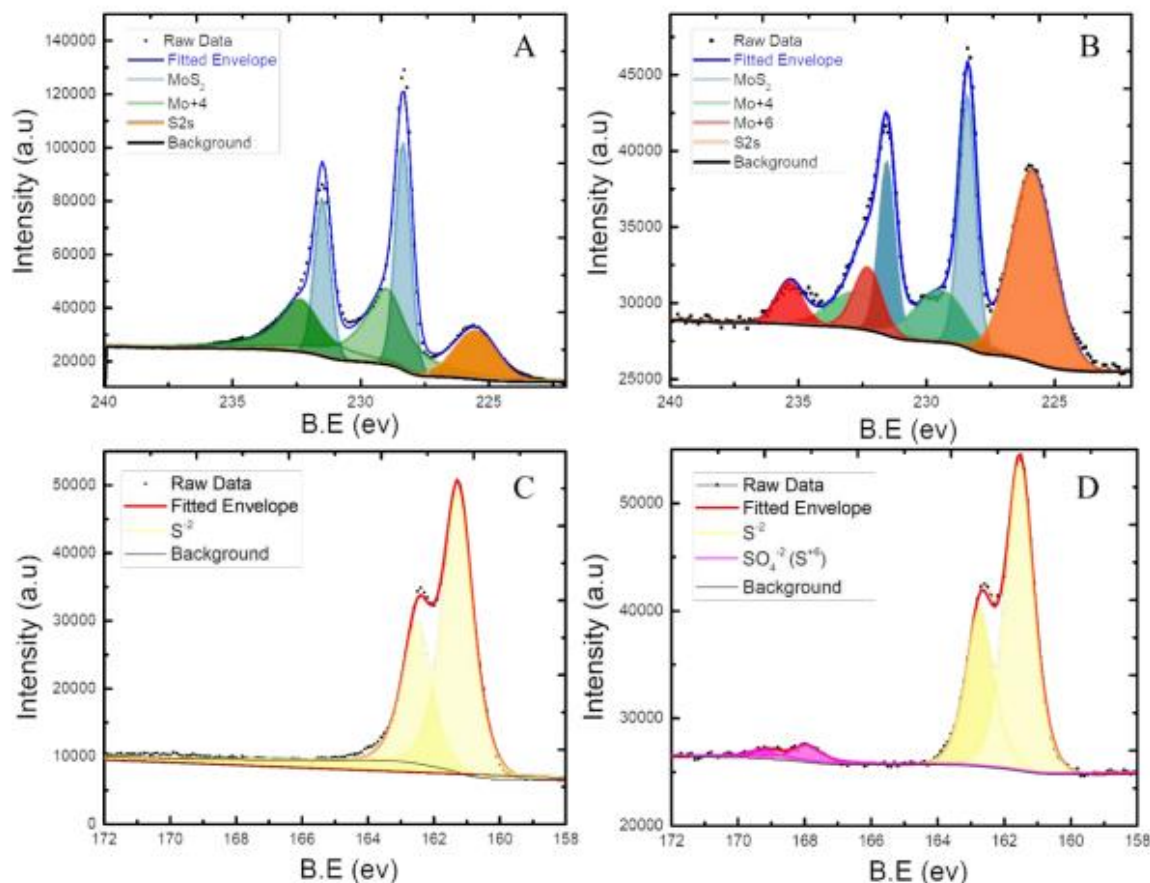


Figure 2: XPS spectra of MoS₂@Al₂O₃ synthesised at 180 °C. Before mercury removal (A,C) is on the left, and mercury removal is on the right (B,D). The spectra for various molybdenum oxidation states are shown in (A,B), and those for various sulphur oxidation states are shown in (C,D) [20]

X-ray Diffraction (XRD)

A material's crystalline phases can be determined using XRD analysis, which also reveals chemical composition details via XRD peaks and planes at 2θ in the XRD diffractogram. For instance, supported alumina was subjected to XRD investigation both before and after Hg was introduced to the gold nanoparticle [21]. The product's XRD prior to Hg treatment showed peaks for 2θ at 38.17° , 44.38° , 64.57° , 77.56° and 81.72° , as well as (111), (200), (220), (311) and (222) planes, respectively. This design showed nanoparticles of gold. Following Hg treatment, the XRD analysis showed peaks for 2θ at 35.62° , 37.47° , 40.44° , 52.59° , 63.74° , 69.64° , 76.51° , 78.37° and 79.94° , as well as 2θ planes at (100), (002), (101), (102), (110), (103), (112), (201), and (004). Au₃Hg was the source of the pattern. It was clear from the pattern of gold nanoparticles before and after they had been exposed to mercury that the gold nanoparticle on supported alumina had been successful in capturing Hg and creating an amalgamation between mercury and gold. Another study [22] treated its samples of 1:3 and 1:6 Ag@MSA with Hg²⁺ solution and then produced an XRD diffractogram. There were also two peaks for the Ag-Hg alloy in sample 1:3 Ag@MSA (b). Samples 1:3 and 1:6 Ag@MSA were also successful at capturing Hg, according to the XRD analyses (refer Figure 3).

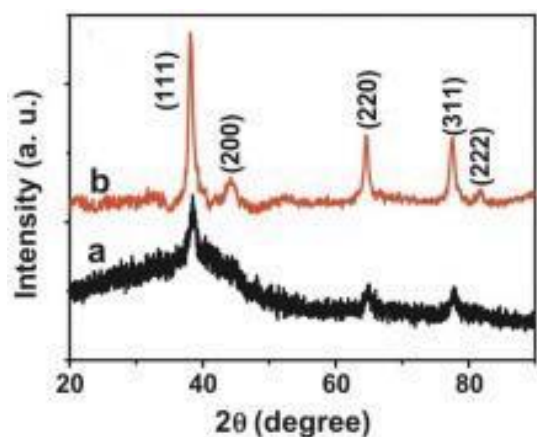


Figure 3: XRD diffractogram after treating the samples (a) 1:6 Ag@MSA and (b) 1:3 with Hg^{2+} solution [22]

Transmission Electron Microscopy (TEM)

TEM is a type of microscopy that can produce images with extremely high resolution down to a level of few Angstroms (or around 0.19 nm). In order to compare the results before and after Hg^{2+} was introduced to the nanoparticles, TEM was used in the study on the removal of mercury ions from water by silver nanoparticles protected by mercaptosuccinic acid (MSA) and supported on activated alumina. The 1:6 Ag@MSA nanoparticles did not exhibit any aggregated mass during the image capture (Figure 4) compared to after the Hg^{2+} was added [22]. Another work that removed Hg from drinking water by using gold nanoparticles based on alumina similarly employed TEM to observe changes before and after Hg adsorption [21]. The research demonstrated that the nanoparticles were uniformly dispersed and spherical in shape prior to adsorption. Many bigger particles were surrounded by smaller ones after adsorption. The investigation came to the conclusion that when Hg adsorption occurred, the protective group that formed the ionic shell was damaged.

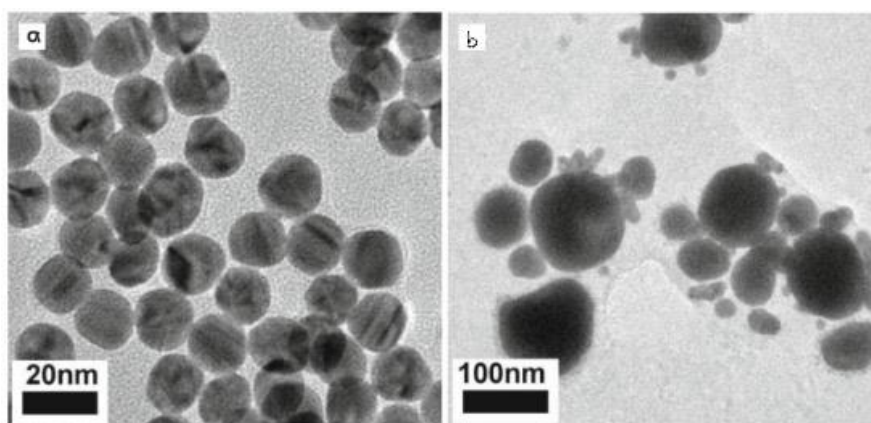


Figure 4: TEM image of gold nanoparticles (a) before and (b) after mercury adsorption [21]

Thiol as Adsorbent

Thiol is a group that contains -SH functional group [23]. Heavy metals and sulphur (S) bind to one other very well. To give the surface of the catalyst, thiol compounds are typically

combined with materials such alumina, Au, organic polymers, and silica [24]. Thiol-containing adsorbents can absorb mercury through covalent bonds. As illustrated in Figure 5, thanks to the link created by the sharing of electron pairs between Hg (soft acid) and S (soft base), thiol group and Hg^{2+} can form a stable complex. In order to effectively remove the soluble Hg^{2+} in water, the complex that is generated must be poorly soluble. Several of the thiols utilised in earlier investigations as mercury adsorbents are displayed in Table 4 below. These features are crucial for exhibiting strong Hg^{2+} adsorption: a large concentration of S binding sites, evenly distributed and accessible S groups, and a high porous volume [25].

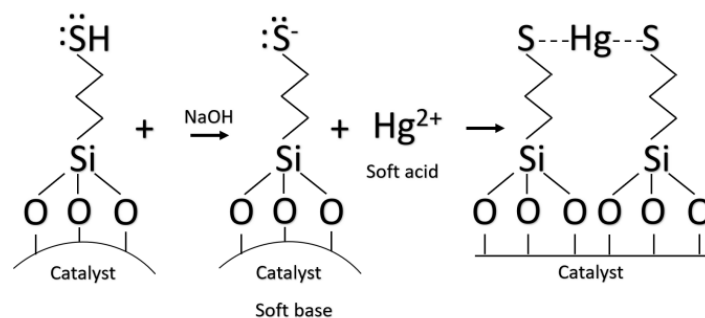


Figure 5: Schematic diagram of how thiol (soft base) adsorbs Hg^{2+} (soft acid) in wastewater.

Table 4: Thiols for Hg^{2+} adsorption.

Thiol	Product	Outcome	Reference
MPTMS	Thiol-functionalised silica ($\text{SiO}_2\text{-SH}$)	377.36 mg g^{-1} maximum adsorption capacity at 293 K.	[3]
Cysteamine	PVDF-PAA membrane	94.1 $\pm$ 1.1 % for IE method and 99.1 $\pm$ 0.1 % for EDC/NHS coupling method.	[23]
Ethanethiol (EDT)	Porous organic polymer (POP)-based adsorbent synthesised from melamine, 4-allyloxybenzaldehyde and EDT, 4AS-MBP adsorbent	98.4% of AE.	[26]
1,2-ethanedithiol	COF-S-SH adsorbent	>99% of AE.	[27]
3-mercaptopropyltrimethoxysilane (MPTMS)	Thiol-functionalised mesoporous silica nanoparticles.	Highest adsorption capacity: 479 mg g^{-1} .	[28]

Characterizations of Thiol for Hg^{2+} Adsorption

The three primary methods described in this section - Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared Spectroscopy (FTIR), and X-ray Photoelectron Spectroscopy—are used to characterise thiol for Hg^{2+} adsorption (XPS).

Field Emission Scanning Electron Microscopy (FESEM)

The surface morphology of the adsorbents has changed both before and after the adsorption procedure, according to FE-SEM examination. The EDX spectra's confirmation of the adsorbed components lends credence to the photos. FE-SEM was utilised to examine the differences between the composite PPy/MAA (thiol-functionalized conducting polypyrrole) before and after Hg^{2+} adsorption (Figure 6). In comparison to following Hg^{2+} adsorption, the composite appeared smoother and with more uniform granular size. Due to the potential for Hg^{2+} to collect on the surface of the composite following Hg^{2+} adsorption, the composite seemed rougher as can be seen in Figure 6. Another mercury peak was visible in the treated composite's EDX spectrum, showing that the mercury had been successfully adsorbed onto the material [29]. In a prior research, Hg^{2+} adsorption on the SBA-15-SH was further explained using SEM and elemental mapping.

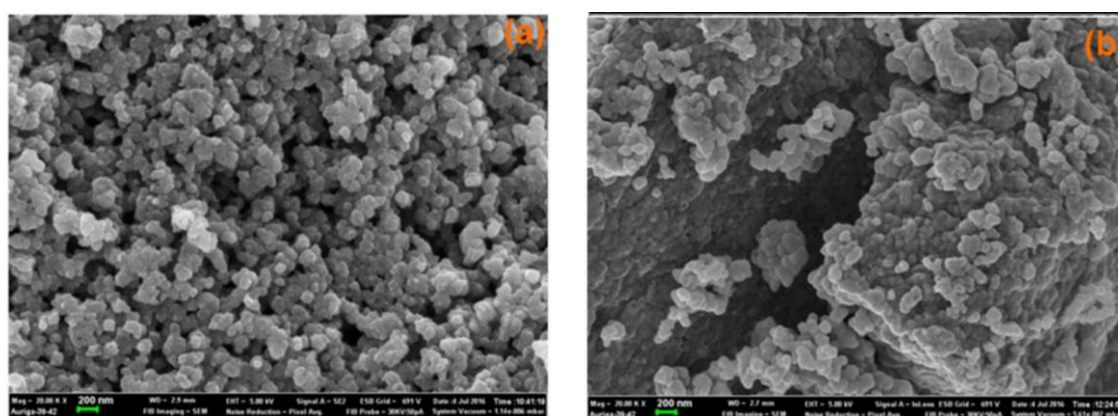


Figure 6: FESEM images of PPy/MAA (a) before and (b) after Hg^{2+} adsorption [29]

Fourier Transform Infrared Spectroscopy (FTIR)

In order to determine whether Hg^{2+} successfully interacted with S-H or not, FTIR is used to detect the presence of thiol groups in the adsorbent. Before evaluating the adsorbent for mercury removal, the data demonstrates the evidence of the typical stretching mode for S-H at 2552 cm^{-1} (COF-S-SH). Following the adsorbent's successful removal of mercury, the FTIR revealed the lack of the S-H characteristic stretching mode (COF-V), indicating that the Hg^{2+} and S-H group successfully interacted between them [27]. According to several research, the distinctive S-H stretching mode can be observed at 2564 cm^{-1} [24] and 2560 cm^{-1} [28].

X-ray Photoelectron Spectroscopy (XPS)

XPS is utilised to study the changes of the element composition and electronic state of the atoms within the adsorbent before and after the adsorption process (Figure 7). It can be seen from Figure 7 that an adsorbent called SiO_2 -SH microspheres was created and the presence or absence of the aforementioned interactions in the SiO_2 -SH was determined using XPS. Given the signal of the XPS at 102.04 and 105.07 eV, which were attributed to the Hg 4f, the investigation concluded that Hg^{2+} presence was present in the SiO_2 -SH. The S 2p XPS spectra revealed a shift in the S binding energy from 163.42 to 163.47 eV upon adsorption. The shift shows that after Hg^{2+} intrusion, significant binding interactions between Hg^{2+} and S in SiO_2 -SH were seen. Binding energy of Si 2p in the SiO_2 -SH are almost the same for both

before and after Hg^{2+} adsorption, which suggested that Hg^{2+} species are not complexed with Si species [3]. Study [23] also said that at peaks Hg 4f_{7/2} and Hg 4f_{5/2}, the binding energies can be read at between 100 and 105 eV (ion exchange) and 102 and 106 eV (EDC/NHS). The signals are also almost same as in [27]. Hence, Hg^{2+} was found successfully bonded to sulphur.

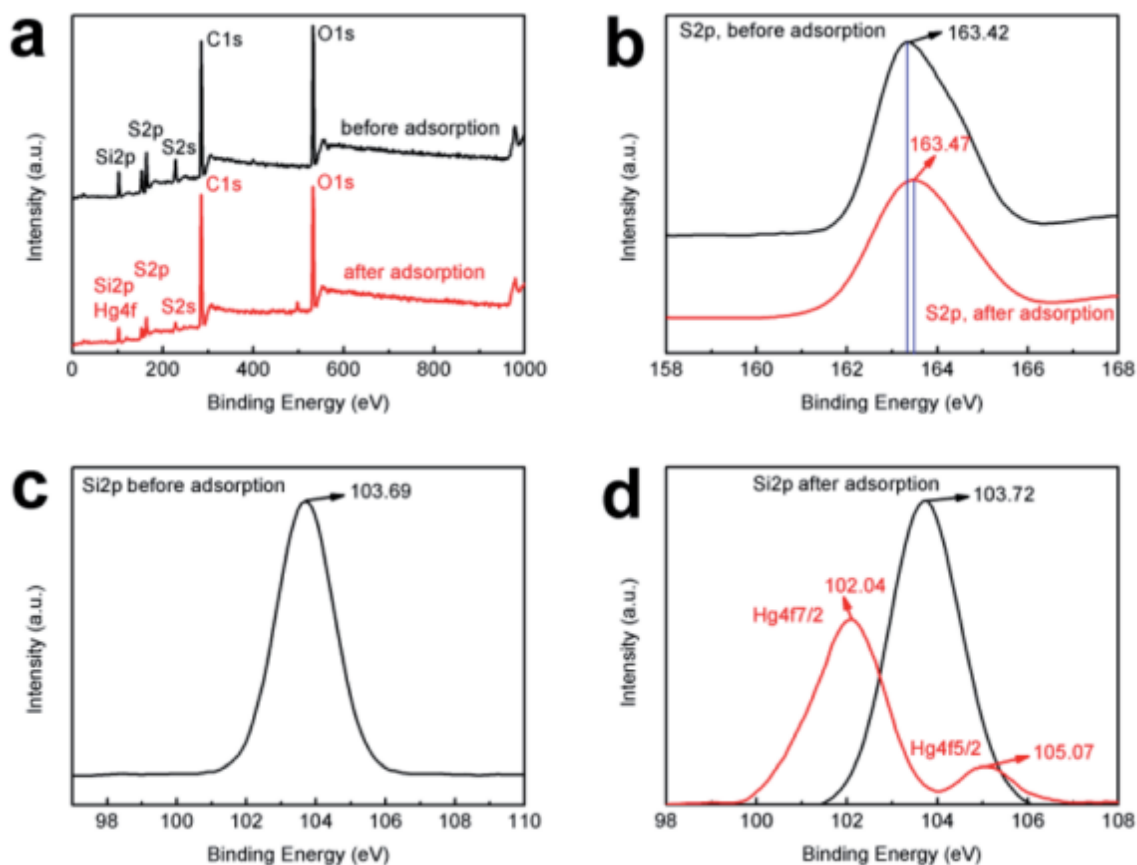


Figure 7: XPS spectra of $\text{SiO}_2\text{-SH}$ microspheres for (a) before and after Hg^{2+} adsorption (adsorption condition: 10 mg of $\text{SiO}_2\text{-SH}$, $C_0 = 200$ mg/L, pH = 5.5, $T = 293$ K, $t = 24$ h) (b) before and after Hg^{2+} adsorption for S 2p (c) before and after Hg^{2+} adsorption for Si 2p and (d) after Hg^{2+} adsorption for Si 2p/Hg. [3].

Conclusions

A reusable adsorbent is good as it can reduce energy used in making it all over again. This review shows that alumina has potential to boost the adsorbent by itself or by composite and γ -alumina has the best potential as adsorbent compared to other alumina phases. Thiols are very important for heavy metals remover especially mercury from water systems. The analysis shown in this review suggests that XPS, XRD, TEM, SEM, and FTIR are the important tools to research element compositions, material morphology, components, surface area and confirmation of bonding molecules. Through the analysis, we found their potentials in the field of study, providing guidelines for future research.

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Author contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of conflict of interest

The authors have no disclosures to declare.

Compliance with ethical standards

The work is compliant with ethical standards.

References

- [1] Shen, Y., Jiang, N., Liu, S., Zheng, C., Wang, X., Huang, T., Guo, Y. & Bai, R. (2018). Thiol Functionalization of Short Channel SBA-15 Through a Safe, Mild and Facile Method and Application for the Removal of Mercury (II). *Journal of Environmental Chemical Engineering*, 6(4), 5420-5433.
- [2] Tuzen, M., Sari, A., Mogaddam, M. R. A., Kaya, S., Katin, K. P. & Altunay, N. (2022). Synthesis of Carbon Modified with Polymer of Diethylenetriamine and Trimesoyl Chloride for the Dual Removal of Hg(II) and Methyl Mercury ($[\text{CH}_3\text{Hg}]^+$) from Wastewater: Theoretical and Experimental Analyses. *Materials Chemistry and Physics*, 277, 125501.
- [3] Liang, R. & Zou, H. (2020). Removal of Aqueous Hg(II) by Thiol-Functionalized Nonporous Silica Microspheres Prepared by One-Step Sol-Gel Method. *RSC Advances*, 10(31), 18534-18542.
- [4] Viltužnik, B., Košak, A., Zub, Y. L. & Lobnik, A. (2013). Removal of Pb(II) Ions from Aqueous Systems Using Thiol-Functionalized Cobalt-Ferrite Magnetic Nanoparticles. *Journal of Sol-Gel Science and Technology*, 68(3), 365-373.
- [5] Yap, P. L., Kabiri, S., Tran, D. N. H. & Losic, D. (2019). Multifunctional Binding Chemistry on Modified Graphene Composite for Selective and Highly Efficient Adsorption of Mercury. *ACS Applied Materials and Interfaces*. 11(6), 1-48.
- [6] Li, S., Xu, H., Wang, L., Ji, L., Li, X., Qu, Z. & Yan, N. (2021). Dual-Functional Sites for Selective Adsorption of Mercury and Arsenic Ions in $[\text{SnS}_4]^{4-}/\text{MgFe-LDH}$ from wastewater. *Journal of Hazardous Materials*, 403, 123940.

- [7] Hu, X., Chen, C., Zhang, D. & Xue, Y. (2021). Kinetics, Isotherm and Chemical Speciation Analysis of Hg (II) Adsorption over Oxygen-Containing MXene Adsorbent. *Chemosphere*, 278, 130206.
- [8] Prabhu, P. P. & Prabhu, B. (2018). A Review On Removal of Heavy Metal Ions from Waste Water using Natural/Modified Bentonite. *MATEC Web of Conference*, 144, 02021.
- [9] Ali, M. E., Hoque, M. E, Safdar Hossain, S. K. & Biswas, M. C. (2020). Nanoadsorbents For Wastewater Treatment: Next Generation Biotechnological Solution. *International Journal of Environmental Science and Technology*, 17, 4095-4132.
- [10] Urbonavicius, M., Varnagiris, S., Pranevicius, L. & Milcius, D. (2020). Production of Gamma Alumina Using Plasma-Treated Aluminum and Water Reaction Byproducts. *Materials*, 13(6), 1–12.
- [11] Paranjpe, K.Y. (2017). Alpha, Beta and Gamma Alumina as a Catalyst -A Review. *The Pharma Innovation Journal*, 6(11), 236-238.
- [12] Zheng, Y., Duan, Y., Tang, H., Li, C., Li, J., Zhu, C. & Liu, S. (2019). Experimental Research on Selective Adsorption of Gaseous Mercury (II) Over SiO₂, TiO₂ and γ -Al₂O₃. *Fuel*, 237, 202-208.
- [13] López-Juárez, R., Razo-Perez, N., Pérez-Juache, T., Hernandez-Cristobal, O. & Reyes-López, S. Y. (2018). Synthesis of α -Al₂O₃ from Aluminum Cans by Wet-Chemical Methods. *Results in Physics*, 11, 1075–1079.
- [14] Wang, X., Zhan, C., Kong, B., Zhu, X., Liu, J., Xu, W., Cai, W. & Wang, H. (2015). Self-Curled Coral-Like Gamma-Al₂O₃ Nanoplates for use as an Adsorbent. *Journal of Colloid and Interface Science*, 453, 244 – 251.
- [15] Huo, Q., Yue, C., Wang, Y., Han, L., Wang, J., Chen, S., Bao, W., Chang., L. & Xie, K. (2020). Effect of Impregnation Sequence of Pd/Ce/ γ -Al₂O₃ Sorbents on Hg⁰ Removal from Coal Derived Fuel Gas. *Chemosphere*, 249, 1-10.
- [16] Mahapatra, A., Mishra, B. G. & Hota, G. (2013). Electrospun Fe₂O₃-Al₂O₃ Nanocomposite Fibers as Efficient Adsorbent for Removal of Heavy Metal Ions from Aqueous Solution. *Journal of Hazardous Materials*, 258-259, 116-123.
- [17] Bawa, S. G., Ahmed, A. S. & Okonkwo, P. C. (2016). The Study of Thermal Effect on the Surface Properties of Gamma-Alumina Synthesised from Kankara Kaolin. *Nigerian Journal of Technology*, 35(1), 66-70.
- [18] Nath, J., Dror, I., Landa, P., Vanek, T., Kaplan-Ashiri, I. & Berkowitz, B. (2018). Synthesis and Characterisation of Isotopically-Labeled Silver, Copper and Zinc Oxide Nanoparticles for Tracing Studies in Plants. *Environmental Pollution*, 242, 1827–1837.
- [19] Derakhshani, M., Hashamzadeh, A. & Amini, M. M. (2018). Novel Synthesis of Mesoporous Crystalline γ -Alumina by Replication of MOF-5-Derived Nanoporous Carbon Template. *Ceramics International*, 44(14), 17102-17106.

- [20] Saias, E., Ismach, A. & Zucker, I. (2022). Engineering the Performance and Stability of Molybdenum Disulfide for Heavy Metal Removal. *ACS Applied Materials & Interfaces*, 2023, 15(5), 6603-6611.
- [21] Lisha, K. P., Anshup & Pradeep, T. (2009). Towards a Practical Solution for Removing Inorganic Mercury from Drinking Water Using Gold Nanoparticles. *Gold Bulletin*, 42, 144–152.
- [22] Sumesh, E., Bootharaju, M. S. & Pradeep, A. T. (2011). A Practical Silver Nanoparticle-based Adsorbent for the Removal of Hg^{2+} from Water. *Journal of Hazardous Materials*, 189(1-2), 450-457.
- [23] Hernández, S., Islam, M. S., Thompson, S., Kearschner, M., Hatakeyama, E., Malekzadeh, N., Hoelen, T. & Bhattacharyya, D. (2020). Thiol-Functionalized Membranes for Mercury Capture from Water. *Industrial and Engineering Chemistry Research*, 59(12), 5287-5295.
- [24] Solis Maldonado, C., Rivera De la Rosa, J., Lucio-Ortiz, C. J., Valente, J. S. & Castaldi, M. J. (2017). Synthesis and Characterisation of Functionalized Alumina Catalysts with Thiol and Sulfonic Groups and Their Performance in Producing 5-Hydroxymethylfurfural from Fructose. *Fuel*, 198, 134-144.
- [25] Yang, Z., Gu, Y., Yuan, B., Tian, Y., Shang, J., Tsang, D. C. W., Liu, M., Gan, L., Mao, S. & Li, L. (2021). Thio-Groups Decorated Covalent Triazine Frameworks for Selective Mercury Removal. *Journal of Hazardous Materials*, 403, 123702.
- [26] Ryu, J., Lee, M. Y., Song, M. G., Baeck, S. H., Shim, S. E. & Qian, Y. (2020). Highly Selective Removal of $\text{Hg}(\text{II})$ Ions from Aqueous Solution using Thiol-Modified Porous Polyaminal-Networked Polymer. *Separation and Purification Technology*, 250, 117120.
- [27] Sun, Q., Aguila, B., Perman, J., Earl, L. D., Abney, C. W., Cheng, Y., Wei, H., Nguyen, N., Wojtas, L. & Ma, S. (2017). Postsynthetically Modified Covalent Organic Frameworks for Efficient and Effective Mercury Removal. *Journal of the American Chemical Society*, 139(7), 2786-2793.
- [28] Yan, X., Meng, J., Hu, X., Feng, R. & Zhou, M. (2019). Synthesis of Thiol-Functionalized Mesoporous Silica Nanoparticles for Adsorption of Hg^{2+} From Aqueous Solution. *Journal of Sol-Gel Science and Technology*, 89(3), 617-622.
- [29] Das, R., Giri, S., Muliwa, A. M. & Maity, A. (2017). High-Performance $\text{Hg}(\text{II})$ Removal Using Thiol-Functionalized Polypyrrole (PPy/MAA) Composite and Effective Catalytic Activity of $\text{Hg}(\text{II})$ -Adsorbed Waste Material, *ACS Sustainable Chemistry & Engineering*, 2017(5), 7524-7536.