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Mercury, a silent killer to human health and environment: A review of India

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Abstract
The present paper reviews information from the existing literature about Mercury (Hg), a silent killer for humans and the ecosystem along with the summary of various Mercury removal techniques for commercial use. Among different Mercury forms, methyl mercury is the most injurious and UNEP stated that Mercury could never be removed from the environment as it may reside up to decades in the form of methylmercury in soil and up to two years in the atmosphere as inorganic elemental Mercury. The dose and rate of exposure to Mercury decide its toxicity and varies with its different form. So, this review focuses on assessing global sources of Hg, including its chemical and physical behaviour in the atmosphere, pathways of Mercury in the context of human health, and economical ideas for reducing all these by adopting techniques. Mercury limit should be 0.2mg/L in water stated by the US Environmental Protection Agency. In the last decade, the Indian population has been exposed to approximately 56.86 tons of Hg as per the UNEP calculation protocol. Mercury limits and standards need to be reestablished and reviewed to control mercury pollution at the source level, keeping in mind the irreversible neurotoxic effects it causes. Drinking-Water authorities need to install specific and reasonable treatment measures in affected and prone areas. Some techniques have shown good efficiency in Mercury removal such as Blue Pro technology, organic powdered activated carbon from the walnut shell, bio adsorption of mercury. The research and development need to be done more on the treatment technologies keeping in mind the climatic conditions and local availability of raw materials in the affected areas.

Keywords: mercury pollution, global sources, pathways, emission scenarios, human health, policy-making, treatment technology

1. Introduction

Heavy metal toxicity is a significant concern among the scientific community. Metals with a density of over five are heavy metal. Mercury (Hg) with a density of 14 is a matter of significant concern. Mercury is found approximately 0.5 ppm in earth crust as elemental mercury or as a sulfide. Mercury has a −38.83 °C freezing point and having a 356.73 °C of boiling point. Atmospheric behavior and contamination of Mercury lead to a global impact on the environment and human beings. Mercury (Hg derived from the Greek word hydrargyrum; hydra-water and argyros- silver) is a silvery fluid having a unique electronic configuration and chemical properties. It is slightly soluble in water and its solubility increases by 1.3 per 10 °C increase in temperature (Gaffney and Marley 2009) [28]. It is a strongly dispersed element, having a complex biogeochemical cycle and bio magnification capacity in the ecosystem food chain.

Naturally, Hg present in two forms, one as a dimeric cation Mercury (I) (Hg_2^+ mercuries ion), and another in the form of Mercury (II) (Hg^+ mercuric ion). Mercury (II) (Hg^+) is the primary pollutant, can cause a great threat to human as its binds with amino acids (Miretzkya and Cirelli 2009). Various forms of Mercury listed in (Table-1) Exposure to organic or elevated mercury in humans causes various neurological and cardiovascular diseases, and, sometimes, it also shows reproductive and immune system disorder (Sundseth *et al*. 2017) [34]. A great threat to humans as it binds with amino acids cysteine. Atmospheric deposition is the major source of mercury. Pollution of mercury is at high risk from discharge sources like the chloralkali industry, mining, pharmaceutical, paint industry. Methylation of Hg^{2+} in the aquatic ecosystem is because of low pH and positive redox potential (Wood 1980) [26].

Atmospheric average resident time of Mercury is 0.8 to 2 years. Due to anthropogenic emission, about 70% of mercury levels increment is marked during the last hundred years (Gaffney and Marley 2014) [27].

The first largest emission source of Mercury is artisanal and small-scale mining followed by the stationary coal combustion, mainly coming from coal power plants. India is among the world's third-largest coal production sector. This coal naturally contains many metals in trace form, including the dangerous amount of heavy metal Mercury in various forms such as inorganic compounds- sulfides (HgS, cinnabar), chlorides, and sulfates depending upon its types and origin.

Local users are the primary concern under contaminated environments as toxicity and exposure duration can cause damages like neurological disorder, developmental, behavioral abnormalities in humans (Fitzgerald and Clarkson 1991; Baeyens *et al*. 1996) [72, 54]. For controlling and monitoring the deterioration of human health and the environment from anthropogenic emissions and the release of Mercury- "UNEP Minamata Convention" has been signed up in 2014 by over 120 nations. Therefore, it is prime time to get knowledge about mercury contamination, their inhalation route in human beings,

and the natural cycle by doing research and development work we can control and mitigate Mercury. In this paper, our prime focus is to review the existing global and local studies on Mercury to understand better: sources, pathways, reservoirs, removal techniques, and potential health hazards with some suitable strategies for the prevention or minimization of Hg pollution.

2. Mercury sources and toxicity

Mercury is one of the most fatal and toxic heavy metals. It can have been derived from many natural and man-made sources. Mercury exists in three forms: elemental, inorganic, and organic (methyl mercury) in the environment. The toxicity depends on its availability in the environment and interaction with human exposure. There is a complex cycle of transportation of mercury within land, water, atmosphere. Much natural availability and anthropogenic activities are Mercury sources like Hg present in cinnabar, natural weathering from the rocks, volcanoes release Mercury in episodic manners, small scale mining of gold, coal-fired plants burning of medical waste, many daily use devices in household activities, fungicide. People are exposed to mercury by consuming shellfish, fish in which methyl mercury is found, or by inhaling accidental mercury release when a material or a device broke down. Mercury can form inorganic salts like chlorine, sulphur, and other elements.

The pathways of mercury are well understood by some recent researcher's models. According to these model's mercury emissions because of primary natural sources are contributing 1/2 or 1/3rd to the total emission in the atmosphere (UNEP 2008).

UNEP emission inventory states that 56% of total Hg global anthropogenic emission contributed from eight countries with the highest emission which are China, India, Indonesia, Columbia, South Africa, Russia, Ghana, and the U.S. which all together ended up by adding up to 1059 Mg/year of Hg in the atmosphere (AMEP/UNEP 2013; UNEP 2013). By the process of re-mobilization mercury is again released in the atmosphere after human use. About 30% of total Hg annual inputs account from the direct anthropogenic sources (re-emission plus total anthropogenic and natural emissions) as shown in Fig 1. To the atmosphere (Pirrone 2010; UNEP 2013; Street *et al*. 2011) [2, 7]. The largest Hg terrestrial pool is soil (Grigal 2003; Obrist 2012) [16, 17]. Through the ocean air-sea exchange process atmospheric concentrations of Hg reservoirs are strongly affected (Soerensen *et al*. 2012) [7].

3. Depicting Emissions by sector

The atmospheric mercury level globally is estimated between 4400 and 5300 Mg. The anthropogenic activities which are continued to affect the major Hg reservoirs such as the aquatic ecosystem (270-450 Gg), terrestrial ecosystem (soil-250-1000 Gg), and atmosphere (4.4-5.3 Gg). 50% of the globally oceanic Hg drain is contributed by India and China into the North Indian Ocean and West Pacific Oceans. These sources are identified from the sector like artisanal and small-scale gold mining activities, cement industry, combustion of coal, and non-ferrous metal through the disposal of mercury-added products, stationery, and ferrous metal production, and other sources (Figure 2). The dominant Mercury releases are reported in 2018 as 837,658 Kg from artisanal and small-scale gold mining (ASGM) followed by stationary combustion of coal by 473,777 Kg (https://www.epa.gov/international/mercury-emmisions-global-context).

Research and Development progress has been going out by analysis and collecting new data from major global Hg reservoirs such as the atmosphere, terrestrial ecosystems, and aquatic ecosystems with techniques and analytical tools so mitigation steps can be carried out with greater efficiency of mercury control and removal. Some recently worked models for Hg are providing wonderful concepts on Hg mitigation such as atmospheric based Hg model (Durnford *et al*. 2012; Horowitz *et al*. 2017) [18, 22], terrestrial Hg model (Semeniuk and Dastoor 2017) [35]. Total gaseous mercury (TGM) is increasing in India and China from coal-based power plants, artisanal, and small-scale gold mining [Slemr *et al*. 2014; Martin *et al*. 2007; Street *et al*. 2011) [20, 39, 15].

4. Environment and Human Health interaction with Mercury

Mercury's impact and exposure are traced out in the atmosphere, aquatic, and terrestrial ecosystem along with exposure and impact on human health.

4.1 Air Pollution

At room temperature metallic mercury exists in liquid form that can evaporate when a device breaks up accidentally releasing into an enclosed space, a small amount of these vapors is enough toxic if inhaled. It is challenging to wash or remove metallic Mercury and its vapors from garments, rugs, furniture, and other permeable items.

Mercury sources are available in most commonly used domestic products, including switches, thermostats, glass thermometers, and bulky appliances. The most commonly used instrument Barometers applied to measure the air pressure have small openings, which create a pathway for Mercury's gradual release. A trace of mercury vapor is present in fluorescent bulbs if released because of unintentional or intentional spills would release metallic Mercury vapors in homes, or it can settle down there on a distinct form of household items, which is difficult to remove (Muehlendahl 1990) [36].

4.2 Water Pollution

Mercury contamination is a primary concern for water. India's river mainly receives effluent from various industries, untreated sewage, agricultural effluent runoff, domestic sewage, and bleach, acid. Intake of infected fish from these contaminated rivers directly causes human health effects. Mercury rapidly moves in the ecosystem food web, whereas; atmospheric Mercury form deposits directly in the aquatic ecosystem.

4.3 Impacts on human health

Mercury adversely affected human health in many terms. It affects our nervous system, endocrine, digestive and reproductive systems.

4.3.1 Nervous System

Nervous system is one of the delicate parts which is getting exposure to Methylmercury and metallic mercury vapors which may directly damage the cell. If methylmercury reaches the brain, it dis-function the nervous system. Higher exposure to all forms of Mercury can impair the brain, kidneys forever, and even it can harm a developing fetus in the womb (Azimi and Moghaddam

2013). Due to high exposure to Mercury, strength reduction in arms and legs have been reported.
Several deadly outcomes of Mercury with the nervous system are seen in terms of protein inhibition, damaged or disrupted neurotransmitters, dysfunction of mitochondria, a damaged framework of neurons structure, destruction of the structural framework of neurons, blindness, and cerebral palsy.

4.3.2 Digestive and Renal Systems
Various digestive disturbances can be caused due to mercury absorption through the epithelial cell as it diminishes the production of the proteolytic enzyme like trypsin, pepsin, chymotrypsin, and xanthine oxidase (Vojani *et al*. 2003). The many problems turn to be noticed due to many health issues that are studied such as ulcers leads to abdominal pain, indigestion, inflammatory bowel disease, and bloody diarrhea, which indirectly facilitates the increase in the quantity of undigested food constituent into the bloodstream (Summers *et al*. 1993) [9].

4.3.3 Endocrine System
Mercury exposure affects the endocrine system, which tends to increase the pituitary, thyroid, adrenal glands, and pancreas problem even as the exposure is less (Rice *et al*. 2014) [37]. Some symptoms like insulin drop, estrogen, testosterone, and adrenaline level affected inside the body due to mercury exposure. The ability to reduce hormone-receptor binding can also be seen because of Mercury exposure that might further weaken endocrine function (Iavicoli *et al*. 2009) [25]. A study found a range of Mercury levels estimated between 6.3 to 77 ppb for the pituitary gland. Another study concluded that mean levels range up to 28 ppb with neurotoxic and cytotoxic effects because of mercury (Nylander and Weiner 1991) [41].

4.3.4 Reproductive System
Mercury exposure is also linked with infertility in both men and women (Dickman *et al* 1998) [42]. Mercury can show several hostile effects on human spermatogenesis, epididymal men sperm count, and testicular weight in men (Cychosz *et al*. 2017) [38]. In females, it includes dropping in estrogen and progesterone levels leading to ovarian dysfunction, which leads to irregular menstruation, ultimately menopause, or maybe tipped uterus is observed in the latter stage (Li *et al*. 2006). Mercury can also hinder the release of the follicle, stimulating hormone and luteinizing hormone from the anterior pituitary, ultimately stimulating menstrual irregularities, including short, long, or irregular cycles with painful cramps reducing the growth for females (Davis 2001) [10].

4.3.5 Fetal toxicity
Spontaneous miscarriage, fetus toxicity, stillbirth, small head, and low birth baby weights are associated with prolonged Mercury exposure (Yoshida 2002) [46]. Methyl mercury traces in blood was moderately related to decreased pregnancy rates (Burbacher *et al*. 1984) [64]. The fetus's brain is where methyl mercury quickly enters via the placenta, and after which, babies might get a variable of congenital disabilities (Finkelman and Tian 2018) [51].

5. Mercury Pollution Scenario
Today, various studies are focusing on Mercury pollution studies In India. One such study is of Sonbhadra District of Uttar Pradesh from where 15 drinking water samples were analyzed, of theses 3 samples (20%) contained Mercury from 0.003–0.026 ppm of Mercury specifically sample number W01, gained from a nearby hand pump at Divulging (0.026 ppm) Mercury, which was 26 times higher Mercury than setting a limit of Mercury for drinking water (0.001 ppm). Similarly, sample numbers W02 (dug well at Annpara) and W06 (hand pump at Chilika Daad) accounted for 0.008 and 0.003 ppm of Mercury, respectively, which is 8 and 3 times higher than the set limit of Mercury for drinking water (Sahu *et al*. 2015) [56].
Aditya Birla Chemicals (India) Ltd. (ABCL), which manufactures chloralkali products, releases their effluent in Dongiya nallah, where Mercury in the water nearby reported as high as 0.176 ± 0.0003 ppm in water (Sahu *et al*. 2015) [56].
Methyl mercury (MeHg) in the fish sample gained from River Ganges from West Bengal location. The study contained 19 species of fish from Ganga River West Bengal; it was inspected, that the muscle of fish shows high levels of Mercury, approximately containing 50-84% of organic mercury. An excellent positive correlation was found between mercury levels to the length of fish (age) and muscle with food habits. *Wallago attu* species owned the highest organic Mercury quantity in their muscles, (0.93 ± 0.61 µg Hg/g) of weight taken as wet weight. At the same time, small-sized fishes like *Puntius sarana, Mystus vittatus, Cirrhinus mrigala, Tilapia mossambicus, Eutropiichthys murius*, was observed below the detection range The MeHg level found in some species of this study indicates that it can activate early nervous system dysfunction, unfavorable impact on human well-being which consumes this.
One of the most prominent Mercury pollution sources is coal combustion at the thermal power plant, as mentioned in Section 1. Hence accounting the levels of Mercury to which the Indian population is exposed becomes crucial. In India, coal is mostly used in thermal power plants. These coal-fired thermal fired power plant sector would release airborne inorganic particles (fly ash and soot), carbon dioxide (CO2), sulphur oxides, chlorofluorocarbons (CFCs), and nitrogen oxides. The Mercury released from the power sector for the last 18 years has been calculated using the following equations.

Mercury in feed = (Coal amount fed to power plants in a year) X (Hg concentration in coal) (1)

The total Coal amount, which is fed to power plants in a year (ton/year) and average Hg concentration in coal (g/ton)) average from table 2.

Emissions factor = (Input factor) X (output spreading factor to air) (2)

Where Input factor = Mercury Input Factor of coal (Hg concentration in coal (g/ton)) taken as average from (table 2) and Output distribution factor for air-limited as 0.9 as per UNEP Tool

Kit for power plants having general electrostatic precipitator (ESP) conditions (Inter 2011).

Estimated Mercury Release (ton/year) = (Activity rate) x (Emissions factor) (3)

The activity rate showed that the coal amount fed to power plants In a year (ton/year), and the emission factor was taken from eq (1). the results for the period 2001 to 2018 are shown in Fig 3.
A study conducted by (Das *et al*. 2015) [66] accounted for direct emissions quantity from one boiler unit of three pulverized coal power plants taken with the boiler unit's unit generation capacities, which were 210MW, 250MW, and 500MW shown in table 3.
Mercury content in coals shows broad distinction; there is a presence of high grade of ambiguity in this estimate since this estimate uses emission factors gained with a low coal sample. It needs to be mentioned that the limit to use a default value of 0.9 for output distribution factor is likely higher than actual values for accounting emissions. Default values (0.9) is an assumption that the volatile Mercury is wholly passed in the flue gas which relies on the efficiency of the air pollution control system installed for this purpose, over 90% is released in the air, and only 10% fraction of the Mercury is retained in solid combustion products. Although these assumptions vary from place to place hence need to be corrected, the definite values are still not sure.

6. Treatment technologies to remove Mercury

6.1 Removal of Mercury using Bacterial Strained Bio Films

In this process wastewater from chlor-alkali plant was examined. In Europe, the total mercury level in several effluent factories ranged between 1.6 to 7.6 mg/liter and chloride concentration was reported as (25g/liter) in those effluents factory wastewater. *Pseudomonas putida* Spi 3 derived and isolated from polluted river sediments used as bacterial strained biofilms here. It can convert ionic mercury to metallic mercury through electrolytic production of chlorine. After this process, we can achieve a 70-98% reduction in mercury reduction. Biofilms of P.putida Spi3 was fed in a bioreactor for biological treatment for aerated chlor-alkali wastewater. Here a pure form of metallic Mercury accumulated in the medium as a result of the microbial reduction process, here in this process as a catalyst microbial biomass help to run the process smoothly without forming a large amount of mercury biomass which overall shows greater adsorption of metallic Mercury. This technique is yet to be used for industrial wastewater treatment trials as some effects of chlorine traced out from chloralkali effluent wastewater treatment. The different salt concentrations needed to check on mercury removal efficiency in the reactor (Canstein *et al* 1994) [24].

6.2 Removal through organic activated carbon

Several carbonaceous materials extracted from organic waste has been used for activated carbon production as commercial activated carbon are very expensive. Bicarbonate treated peanut hulls carbons (BPHC) are 7 times more effective than commercial activated carbon for mercury removal (Namasivayam and Peiasamy 1993). BPHC mercury removal rate is 109.89 mg/g as compared to that of commercial activated carbon with a rate of 12.38 mg/g.
Powdered activated carbon from walnut shell showed adsorption capacity up to 151.5 mg/g which is more economically good for mercury adsorbent in the treatment of industrial liquid stream (Zabihi *et al*. 2010) [43].

6.3 Bio Adsorption of Mercury- Bio adsorption

Mercury removal is obtained through an adsorbent made from Plant coriander (Coriandrum sativum or Chinese parsley). This technique shows 24mg/g adsorption rate when the pH balance lies between 4-10 ranges found in the batch process conducted for 45 minutes and it shows maximum adsorption of 95% efficiency rate at pH range 4-10. This result shows the carboxylic group is effective in adsorption of mercury (Karunasagar *et al*. 2005) [14].

6.4 Removal of Mercury using membrane separation

By using polyethyleneimine a complex polymer for mercury removal, a maximum reduction of mercury of 99% was observed which is represented using the Langmuir model. It shows the highest retention capacity at 311 mg/g by the membrane adsorption. Here adsorption and filtration were done using this complex polymer (Zhang *et al*. 2004) [22].

6.5 Adsorption on modified agriculture and biological wastes

The effective modification of agricultural products is now days used for removing heavy metal like Mercury with a better-enhanced adsorption capacity along with their agricultural by-product. Activated carbon works on the adsorption process (Walterick and Smith 2007; Kumar 2006) [21, 71].
Now days processed vegetables remaining or material rich in minerals such as bicarbonate-treated peanut hull carbon (BPHC) are used effectively as low-cost absorbent; some alternatives are modified to use for this process, like Hardwicikia binata bark (MHBB) (Kumar 2006) [72]. In this review, we trace down a list of the adsorbent for mercury removal from wastewater with a broad exposure of agricultural products, which are cost-effective along with their by-product in table 4.
Using rice husk ash is studied, which is an agricultural waste to check the potential of Mercury's adsorption from aqueous water. The base was pH, particle size, and ionic strength, which leads to being a suitable adsorbent for Mercury. The rice husk ash is finer particles with high pH value lower the concentration of electrolyte and potassium nitrate solution, which is a must fit for adsorption. All this was studied by equilibrium data (Feng *et al*. 2004) [53].

6.6 Removal of Mercury Blue PRO reactive filtration process

Dissolved species of Mercury can be removed using Blue PRO reactive filtration by using several removal steps that lower down particulate. Blue PRO capable of overcoming the limitation of diffusion by filtering of particulates continuous and simultaneously lowering mercury concentration by using an adsorptive media Hydrous ferric oxide (HFO) to ultra-low levels, it requires a continuous backwash filter as it a cost-effective process rather than other tertiary expensive treatment to lower the mercury level. It cheaper and feasible than reverse osmosis, commercial or granular activated carbon method, membrane method, and coagulation system (Shafeeq *et al*. 2012) [6]. Fig 4 shows the design of a typical reactor.

6.7 Removal of Mercury by Reverse Osmosis

Reverse osmosis is used for mercury removal as this system comprises granular activated carbon with a pre-filter tank referred to as a storage tank compartment, a faucet for lowering liquid stream concentration. Many studies followed to check the viability of using reverse osmosis for mercury removal using a flat sheet membrane rather than the typical membrane used in R.O. process like thin-film composite (TFC) or Cellulose Triacetate (CTA) at pH 2-7 of 30mg/L concentration of feed solution to concentrate Mercury from the aqueous stream (Mullet 2009) [44]. The membrane used for this process has a high

rejection rate, which costs up to 5% per gallons of pure water (Shafeeq *et al*. 2012) [6].

A 0.2 to 70 mg/L downfall of Mercury is observed when Mercury is removed through ion exchange and up to 1 to 5µg/L in a full-scale ion exchange process (Ritter and Bibler 1992) [30].

6.8 Ion Exchange Treatment

The ion exchange process has been a widely used process for wastewater treatment. This technique can also be used for mercury removal from aqueous solutions. Anion exchange resins are useful to treat mercury removal in the form of ($HgCl_3$), which is anionic complexes. Cationic exchange resin is not used as it exchanges with copper and cobalt rather than mercury as copper and cobalt contain the iminodiacetic group, which selectively exchanges calcium and magnesium. It results in no effective Mercury removal or adsorption (Patternson 1997). Duolite GT-73 is an ion exchange resin used for mercury reduction in wastewater to less than 10 ppb at Savannah River Site (Ritter and Bibler 1992) [30].

A packed column Ion-exchange processes are usually employed. Usually, for complete ion exchange cycle is operated in four steps, i.e., service, backwash, regeneration, and rinse [46].

The treatment is workable if used to treat low effluent mercury concentration; it shows limitation when water with high total dissolved increases with high solid content. Anions resin exchange technique is preferred as Mercury presents in concentration in chloride the negatively charged complex mercury in wastewater is high chloride is detected (Chlor-alkali plant) for removal of inorganic Mercury (Sorg and Logsdon 1979) [67]. Dowex-50W-X8 and Amberlite IR-120 certain cation exchange resins are used effectively to treat Mercury present in industrial wastewater in the form of the ion exchange technique (Patterson 1997).

6.9 Removal of Mercury using photo catalysis

Removal of carbon through TiO_2- sewage sludge carbon (modified). It provides a photocatalytic removal of mercury. From municipal sewage sludge, activated carbon has been developed using $ZnCl_2$ combined with TiO_2 which will act as chemical activation agents. When TiO_2 combined with $ZnCl_2$ where methanol will be added too can show 5% more adsorption of mercury. Hence photocatalytic removal of mercury is done (Zhang *et al*. 2004) [22].

6.10 Removal of Mercury using Nanoparticle

Alumina nanoparticle is used for mercury removal. It was prepared using the sol-gel method. In this process, alumina sol flocculation was formed by feeding a different amount of mercury until it reaches the concentration level. By using atomic absorption spectroscopy, we can observe mercury ions adsorbed on alumina sols. Results show it decreased up to 1 ppb from 50 to 100 ppm from an initial mercury concentration level (Pacheco *et al* 2006) [59].

6.11 Bolkem Process- Chemical Precipitation for removal of Mercury

When the sulfuric acid (H_2SO_4) is used to react with mercury it Forms Mercury (II) sulfate ($HgSO_4$) by capturing those mercuries. The first step involved lowering the temperature up to 50°C so 80% of H_2SO_4 acid can be concentrated. The second step of the process required a conventional tower that needs to operate with a 93% H_2SO_4 requirement. After both step mercury reaction with acids yields Mercurous sulfate, which is shown below:

$$H_gSO_4 + Hg \rightarrow Hg_2SO_4 \quad (4)$$

This is a very affordable and simple method using which we can easily carry out mercury removal (Shafeeq *et al*. 2012) [6].

6.12 Sulfide Precipitation

The technique where sulfur reacts with the Hg to form crystalline mercury sulfide (HgS) which needs less than 85% H_2SO_4 concentrated acid form. Higher acid concentrations yield more oxidation to form sulfur dioxide (SO_2) from sulfur.

$$H_2SO_4 + Na_2S_2O_3 \rightarrow S + Na_2SO_4 + H_2O + SO_2 \quad (5)$$

A non-desirable acid product comes out as sodium sulfate. The production of Sodium thiosulfate ($Na_2S_2O_3$) must be controlled. The level of mercury sulfide (HgS) needs to be controlled when it is released because it is difficult to remove if generated more than required. We can control the concentration from 15 ppm to 0.5 ppm at neutral pH in the estimated 1 hour.

Precipitation of Mercury occurs because of sulfide (Hydrogen Sulphides), along with other metal that is present as an essential source. In this process, sodium sulfide is not the desired product of acid. All this process lowers down to the pH level, which is already above 9. Better efficiency is observed in the Chlor-alkali plant marked up to 95 to 99% (Shafeeq *et al*. 2012) [6].

6.13 Toho Process

Mercury is separated using potassium iodide, where Mercury along with potassium iodide is used to precipitating mercuric iodide as shown below:

$$2KI + 3H_2SO_4 \rightarrow I_2 + 2KHSO_4 + SO_2 + 2H_2O \quad (6)$$

$$Hg + I_2 \rightarrow HgI_2 \quad (7)$$

This process could also be carried out using cuprous iodine, which forms stable precipitation of Cu_2HgI_4. After this, by using filtration, the desired separation of Mercury is achieved (Lee and Park 2003; Lee *et al*. 2004; Mullet *et al* 2007) [61, 62, 45]; Zabihi *et al*. 2010) [43]. Additionally, Sulphur and iodine in the acid can be removed using air. In this process, we achieved the removal of Mercury from 60 ppm to 1 ppm. The outstanding performance is observed when high acid concentration and low-temperature conditions are present to carry out the process.

6.14 Removal of Mercury by using some flocculants

A chemical coagulant that is used to form aggregate/flocs of smaller solid particles in a liquid is known as flocculants. For improving the sedimentation of smaller particles applied in wastewater treatment, flocculants are widely applied for small particles' filterability. Water turbidity is a significant problem caused by mercury spreading where flocculants could be applied in wastewater treatment to get rid of this issue. Insoluble hydroxides are produced to get a favorable condition like pH, temperature, etc., which helps to produce many cations and

complexes to form long chains on precipitation, which can trap small particles to form a bigger floc (Shafeeq *et al*. 2012) [6].
Mercaptoacetyl poly (ethyleneimine) (MAPEI) is known as a heavy metal flocculent, which is a water-soluble macromolecule and can be synthesized with the reaction of polyethylene mine (PEI) with thioglycolic acid (TGA).
Several conditions required for proper removal rates like increase in pH of PEI molecular weight, chloride ions (Cl^-) and nitrate (NO^{3-}) ions, alkali metal and alkaline-earth metal ions, all this can have benefitted in the removal of turbidity and mercury ions from wastewater with a synergic removal of both effectively (Min *et al*. 2010).

7. Comparisons between treatments available for mercury reduction

Adsorption has advantages as it is sludge free, which is economically feasible and sludge free environment from reverse osmosis and ion exchange as it includes high investment inland and on operational cost (Vraraghavan and Dranamraju 1993). In this review, we discussed many techniques for the removal of mercury either by using agricultural by-products or by using chemical engineering methods. We can state that membrane separation which yields 99% Mercury removal is an upcoming major technique that can be followed for mercury removal followed by using cheap Mercury removal method using activated carbon from agricultural waste like coirpith (154 mg/g), activated carbon from the walnut shell (151.5 mg/g), sugarcane bagasse (35.71 mg/g) rather than using commercial activated carbon. In India studied the Chlor-alkali industry from 2000 to 2004 reported that the Mercury's replacement through the membrane method reduced emissions in the related industry from 123 tons to 6.2 ton (from 2000 to 2004) (Mukherjee *et al*. 2009) [2].

8 Conclusion

In this review, we understand Mercury's global cycling, environmental impacts, human exposure toxicity, environmental reservoirs. Many techniques and case studies are examined to get a more effective way of eliminating and mitigating Mercury from surrounding.
Global changes such as climate change, Hg exchange between terrestrial systems and the ocean, and Hg emissions in the atmosphere can affect concentrations of Hg in nonlinear ways, Mercury is a toxic pervasive pollutant but we cannot avoid it exposure because it used in almost every common used device like automotive parts, batteries, cosmetics, dental amalgams, barometer, thermometers these are used in a limited amount. It not only harms the environment but also affects human beings in the form of several diseases, which leaves its long-lasting impression for many decades. Society needs proper guidance on how it can minimize and reduce mercury uses and exposure surrounds them. Like Mercury, heavy metals are dangerous because they tend to bio accumulate in different forms using different media to travel from one boundary to another. Drinking-Water authorities need to install specific and economical treatment measures in affected and prone areas. Low costs adsorbents and adsorption techniques must be environmentally friendly, economically workable in manufacturing as well as operational level. Activated charcoal using various agricultural by-products showed the valuable result as an adsorbent for mercury, from the last few decades membrane processes removal methods has become a very promising technology. However, still more research is required for the removal process with cost-effective and high efficiency along with process stability level because this pervasive pollutant which needs to be reduced in upcoming decades.

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Table 1: Different forms of inorganic and organic Mercury (Neustad and Pieczenik 2007)

SI No.	Inorganic	Organic
1	Mercuric Chloride	Ethyl mercury
2	Mercuric Iodide	Methyl mercury
3	Mercuric oxide	Merbromin
4	Mercuric sulphide	Merthiolate
5	Mercuric Chloride	Phenyl mercuric salts

Table 2: Average mercury content in coal samples of India (Ds *et al*. 2015)

Sl No.	Coal Source (Air Dried Basis)	Hg g/ton
1.	CCL (Central Coalfields Ltd)	0.22
2.	BCCL (Bharat Cooking Coal Ltd)	0.08
3.	MCL (Mahanadi Coalfields Ltd)	0.20
4.	NCL (Northern coalfields Ltd)	0.06
5.	WCL (Western Coalfields Ltd)	0.12
6.	ECL (Eastern Coalfields Ltd)	0.08
7.	SECL (Southeastern Coalfields Ltd)	0.10
8.	SCCL (Singareni Collieries Company)	0.12

Table 3: Mercury concentrations reported in Flue gas and combustion products (Das *et al*. 2015) [66]

Power plant Unit Capacity (MW)	LOI* of Fly ash (Wt. %)	Solid Products Mercury concentration (dry basis)				Flue gas (µg/Nm^3)	Speciation		Fraction of Hg emitted (average)
		Fly ash (g/t)	Bottom Ash (g/t)	Mill Rejects (g/t)	SPM (g/t)		Hg^{2+}%	Hg^0%	
500	0.64	0.097	0.006	-	0.066	14.84	30.8	60.1	0.81
210	0.85	0.158	0.011	1.373	0.057	11.50	11.3	88.1	0.61
250	2.05	0.242	0.017	0.143	0.105	4.24	41.6	58.1	0.27

(*LOI = loss of ignition)

Table 4: Hg^{2+} adsorption capacity (mg/g) by using different agricultural products and by-products

S. N.	Material	Adsorption capacity of Hg^{2+} (mg/g)	References
	Douglas fir bark	100	(Masri *et al*. 1974) [47]
	Activated pine bark	400	(Vasconcelos and Beca 1994) [40]
	Redwood bark	250	(Masri *et al*. 1974) [47]
	Sulfuric acid lignin	150	(Masri *et al*. 1974) [47]
	Xanthate sawdust	30.1	(Flynn *et al*. 1980) [13]
	Rastunsuo dust	16.2	(Tumnavuori and Aho 1980) [32]
	Dry redwood leaves	175	(Masri *et al*. 1974) [47]
	Dyed bamboo pulp	15.6	(Shukla and Skhardande 1992) [63]

	Undyed bamboo pulp	9.2	(Shukla and Skhardande 1992) [63]
	Dyed jute	13.7	(Shukla and Skhardande 1992) [63]
	Dyed sawdust	18.0	(Shukla and Skhardande 1992) [63]
	Modified wool	632	(Masri *et al*. 1974) [47]
	Undyed sawdust	8.5	(Shukla and Skhardande 1992) [63]
	Rice husk ash	66.66	(Kumar and Bandyopadhyay 2006) [72]
	Modified hardwickia binate bark	21	(Deashkar *et al*. 1990)
	Bark	400	(Randall *et al*. 1974) [33]
	Xanthane	1.149	(Flynn *et al*. 1980) [13]
	CEPI cotton	1000	(Robert and Rowland 1973) [19]
	Palm Shell Powder	20	(Kushwaha *et al*. 2008) [64]
	Activated carbon from mango kernel	7.13	(Somayajula *et al* 2013) [4]
	Activated carbon from Rosamarinus Officinalis Leaves	19.76	(Erhayem *et al*. 2015) [48]
	Peel Biomass of Pachira Aquatica Aubl	-	(Santana *et al*. 2016) [5]
	Coal fly ash	0.44	(Attari *et al*. 2017) [49]
	Roasted Date Palm	282	(Al-Ghouti *et al*. 2018) [50]
	Activated carbon	120	(Al-Ghouti *et al*. 2018) [50]
	Sulphur Modified Roasted Date Pits	280	(Al-Ghouti *et al*. 2018) [50]
	Silane Modified Roasted Date Pits	90	(Al-Ghouti *et al*. 2018) [50]

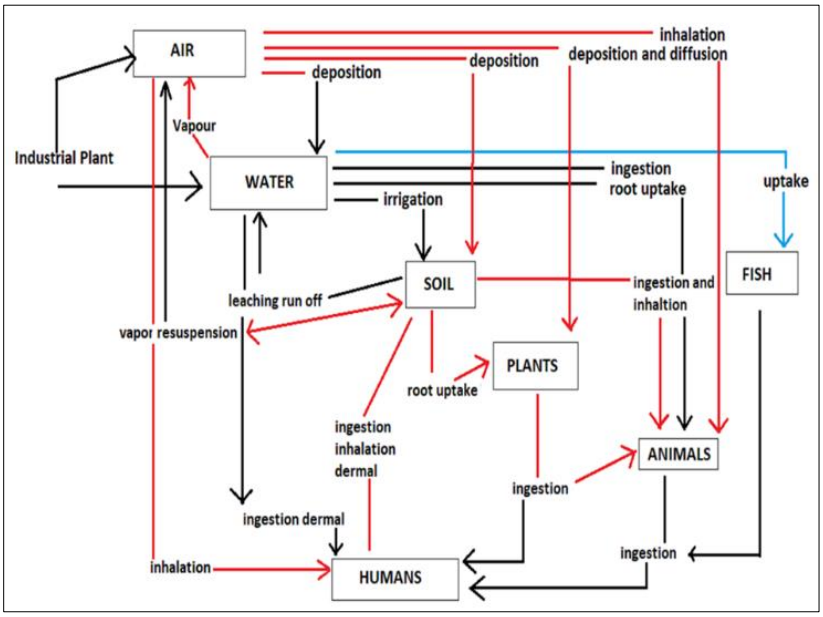

Fig 1: Mercury pathways: Sources, transport, deposition and reaching to humans being (Peirce)

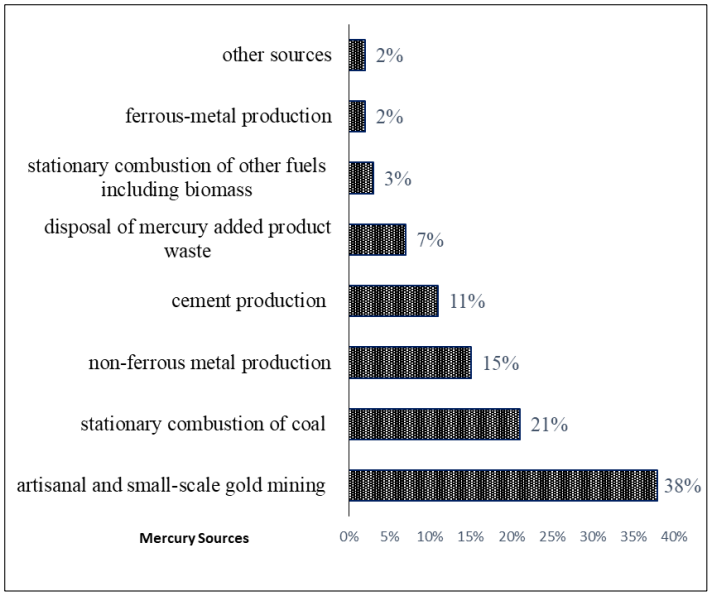

Fig 2: Diverse sources of Mercury pollution [75]

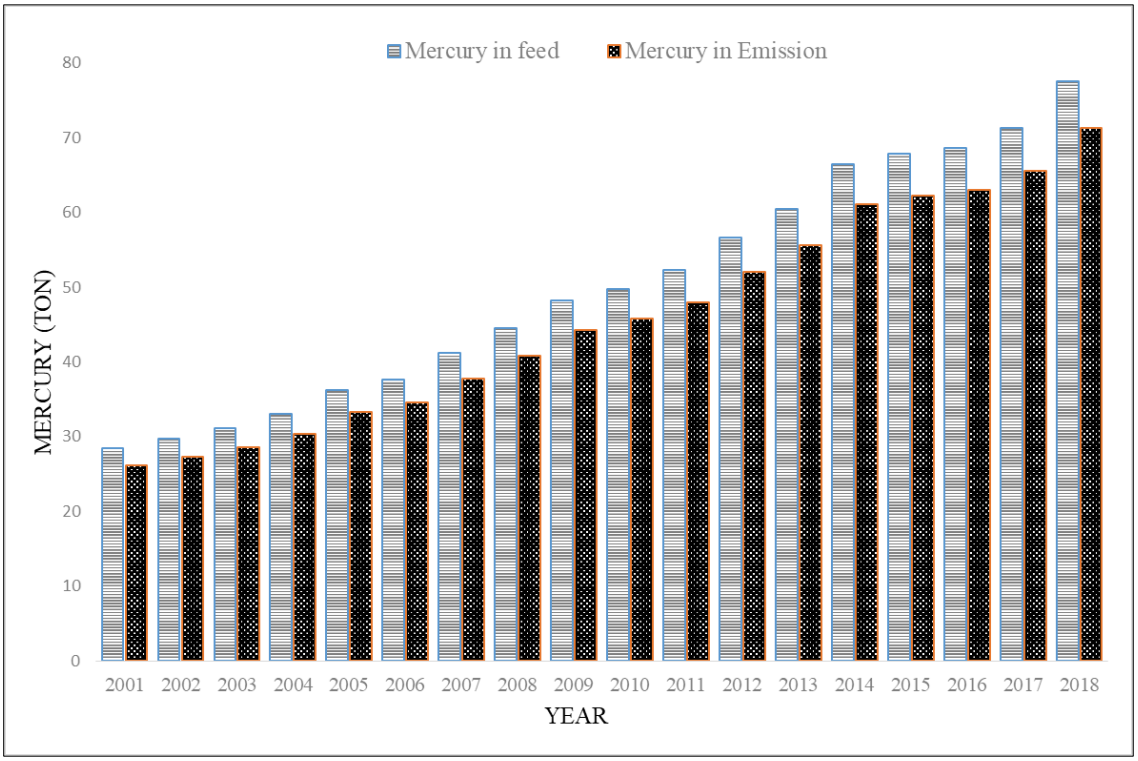

Fig 3: Mercury in coal feed and estimated emissions from the power plant (Coal usage data [76])

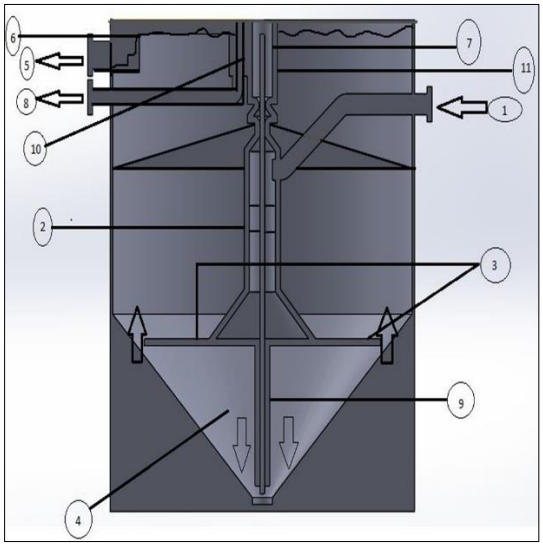

Fig 4: Layout of a typical Blue Pro system [77]

1-Influent; 2- Central Feed Chamber; 3-Radial Arms; 4-Spherical Silica Media; 5- Filtrate; 6- Fixed Effluent Weir; 7-Wash box; 8- Reject Stream; 9-Airlift; 10-Adjustable Reject Weir; 11- Tortuous Path

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