



METHOD FOR TREATING METHYL HG CONTAMINATED WATER AND SOIL OF HINDON RIVER USING EARTHWORM (AS BIOINDICATOR) AND FLYASH, BIOMASS & ALGAE (AS ADSORBENT)

Dr. Pankaj Singh¹, Dr Shilpi Singh², Dr. Gaurav Kumar Rastogi³, Dr.
Vivek Singh⁴, Dr. Abhishek Singh⁵, Shruti Singh⁶

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Abstract

Mercury contamination in water, soil and air is associated with potential toxicity to humans and ecosystems. Industrial activities (Carbon Continental Company –LalKua-Nainital) such as coal combustion have led to increased mercury (Hg) concentrations in different environmental media. This review critically evaluates recent developments in technological approaches for the remediation of Hg contaminated soil, water and air, with a focus on emerging materials and innovative technologies. Based on approaches including adsorption/desorption, oxidation/reduction and stabilization/containment, the performances of innovative technologies with the aid of these materials were examined. In addition, technologies involving organisms, such as phytoremediation, algae-based mercury removal, microbial reduction and constructed wetlands, were also reviewed, and the role of organisms, especially microorganisms, in these techniques are illustrated. Earthworm intensified the organic loading of wastewater in vermifilter soil bed by the fact that it granulates the clay particles thus increasing the hydraulic conductivity of the system.

Keywords: Hg (II), Methyl mercury, Elemental mercury, Remediation techniques, Novel materials, Earthworm (E. Feotida), flyash, Algae and Biomass.

¹Professor and Head – Department of Research, R D Engineering College, Ghaziabad, U.P., India, -201006,

²Associate Professor – Department of Management, Noida International University, Greater Noida, U.P., India,

³Associate Professor – Department of Applied Science, R D Engineering College, Ghaziabad, U.P., India -201006

⁴Associate Professor – Department of Botany- U. P. College, Varanasi, U.P.,

⁵Associate Professor – Department of Chemistry- U. P. College, Varanasi, U.P.

⁶Student – MD 1st Year, -Doctor of Medicine - Jonalta School of Medicine, University of Perpetual Help System Dalta, Phillipines-1740

Email: ¹p.mnavy@gmail.com, ²shilpi.singh@niu.edu.in, ³drgauravrdec@gmail.com, ⁴vivekjnp@gmail.com, ⁵abhupc@gmail.com

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1. Introduction

Mercury (Hg) is a toxic heavy metal that has been regarded as one of the “ten leading chemicals of concern” (WHO, 2017). According to the United Nations Environment Programme (UNEP) report (UNEP, 2018), it is estimated that global mercury emissions to air from anthropogenic sources in 2015 were about 2220 tons. Among the anthropogenic sources, stationary combustion of fossil fuels accounts for 24% of the estimated emissions, primarily from coal-burning (21%) (UNEP, 2018). Other anthropogenic sources include cement production (Wang et al., 2016b), iron and steel production (Wang et al., 2016a), nonferrous metal smelting (Wu et al., 2017b), gold production (Wu et al., 2018b), chlor-alkali industry (Busto et al., 2011, Busto et al., 2013, Kakareka and Kukharchyk, 2012), waste disposal (Pehneck et al., 2010) as well as direct production of mercury. Mercury contamination is of significant concern worldwide owing to its toxic effect on human health (Beckers and Rinklebe, 2017). Among the forms of inorganic mercury, the mercuric cation, Hg^{2+} , has proven to be a predominant toxic agent that can cause damage to kidney and lung (Clarkson and Magos, 2006). Once transformed into its organomercuric forms such as methylmercury (MeHg), Hg acts as a potent neurotoxin which impairs brain function. Apart from the high toxicity of this form of mercury, it has raised particular concern for its capability to biomagnify up the food chain (He et al., 2015, O'Connor et al., 2019, Selin, 2009).

Once emitted to the atmosphere, Hg can be transported and thoroughly mixed in its elemental form $[\text{Hg}(0)]$. The major sink of elemental mercury is deposition to soil or water bodies after oxidation to divalent mercury $[\text{Hg}(\text{II})]$ (Fig. 1) (O'Connor et al., 2019, Selin, 2009). Aside from deposition, point sources of mercury contamination are the predominant cause of Hg pollution in soil and water. Like other heavy metals, mercury cannot be degraded in ecosystems, and therefore remediation should be based on removal or immobilization processes (Fig. 2). Removal technologies involve the mechanism of adsorption, desorption, oxidation and reduction. The major aim of these technologies is to separate mercury from the contaminated media or transform toxic mercury species into less toxic ones (Lewis et al., 2016). The most widely adopted immobilization techniques are stabilization and containment, which prevent mercury migration by chemical complexation or physical trapping, respectively (He et al., 2015).

It is a case study of **Carbon Continental company (Lal-Kua, Ghaziabad)** who is leading world producer of Carbon and that carbon when comes contact with silica Gnerate so much dangerous mineral i.e. Methyl Hg who pollute Hindon River. It is so much dangerous if pregnant lady inhale this contaminated mixed water then either we keep her in a excellect equipped hospital but the born baby will be in deformed shape and even 200-300 villeges who was max depend water from hindon river source facing lots of diseases by this contaminated water

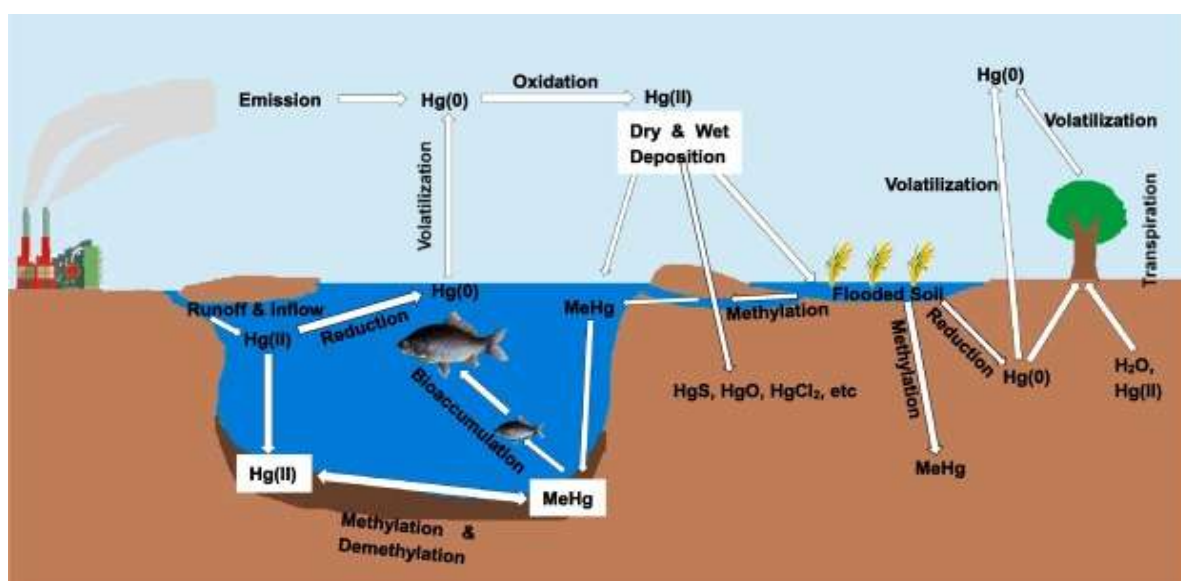


Fig. 1. Inter-phase transfer and transport of mercury in soil, water and air. Acronyms: $\text{Hg}(0)$, elemental mercury; $\text{Hg}(\text{II})$, divalent mercury; MeHg, methylmercury.

There are many Methods which is used for methyl Hg contaminated water treatment:-

1. Distillation, aqueous Ethylation, Purge and temperature and Cold vapor atomic fluorescence spectrometry.

It is designed for determination of CH₃Hg in the range of 0.025 ng/l and may be extended to higher levels by selection of smaller sample size for MDL(Method detection limit) for CH₃Hg has been determined to be 0.02 ng/l when no background elements or interference are present. Minimum level = 0.06 ng/l. MDL as low as 0.009 ng/l can be achieved for low CH₃Hg sample by using extra caution in sample handling and reagent selection, particularly the use of “for ultra-low level only” distillation equipment.

Clean and ultra clear:- reduced or eliminate contamination in trace metal determination .

2. Laser Induced breakdown spectroscopy – (LIBS) for rapid remote measurement method for detection of metals in Environment.

3. Detection of Mercury compounds using Invertase-Glucose Oxidase-based biosensors.(Detected Hg Compound directly in aqueous solution in the range (2-10 ppb).

4. Determination o total Mercury in Coal:
- Due to extreme volatility during coal combustion and its potential to be toxic if released in environment.

Radiochemical neutron activation analysis method based on Pyrolysis followed by double gold amalgamation. During Pyrolysis, volatile elements i.e. Hg and selenium are liberated, and the mercury is preferentially collected by amalgamation with the Gold.

5. Mist Chamber scrubber and Ion – Exchange membrane technologies – Indicating atmospheric (Hg-II) level approx 0.01-0.1 ng/m³.

Now Come To Our Main Work on treatment of Methyl Hg contaminated water With The Earthworm

Eartworms as Bio-indicators of Mercury Pollution –

Bioindicators play an important role in identifying the factor controlling Hg toxicity and bioavailability and can ultimately be used to evaluate hazardous situation.

Bio-indicators provide a pollutant measurement which can be compared with an instrument measurement. Bio-Indicators provide information on the quality of the environment and the actual condition of an organism or Ecosystem, effectively a snap shot often Ecosystem’s health.

Bio-indicators are living organism i.e. plants, planktons, animals and Microbes, which are utilized to screen the health of the natural ecosystem in the environment. They are used for assessing environment health and bio-geographic changes taking place in the environment

Earthworms are simple ,well-studied creatures that can quickly provide indication of bioavailability at relatively low cost. A methodology using the earthworm **Eisenia fetida** has been developed to evaluate the bioavailability of Hg in mining tailing and aqueous solutions. Result indicates that **E.Fetida** do accumulate Hg and positive correlation exist between Hg concentration in worm tissues, the substrate they consume and length of exposure. To investigate the effect of natural organic acid as mediators of Hg bioavailability, metallic Hg was dissolved in tannic acid and fed to the worms in a substrate of Paper and silica sand. Total Hg and methyl Hg was analyzed to determine whether methylation of Hg was occurring in the substrate ,directly within the worms(ex - in intestine) or in the tannic acid-Hg solution and the substrate particularly significant in dark water system ,where naturally occurring organic acid may be facilitating methylation internally within organism.

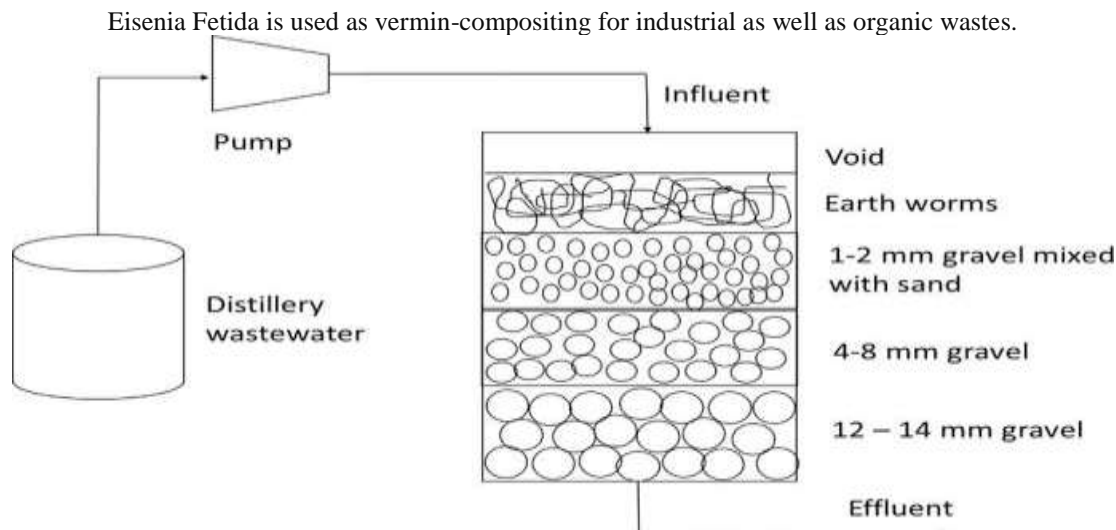
There is some other reason becoz Methyl mercury might be easily absorb and accumulated in earthworm becoz of its lipid solubility.

Earthworm body works as a boifilter and they have been found to remove the 5 days BOD(BOD5) by over 90%,COD by 80-90%,total dissolved soilds(TDS) by 90-92% and the total suspended solid(TSS) by 90-95% from waste water by the general **Mechanism of ingestion and biodegradation** of organic waste ,heavy metals and solids from wastewater and also by their absorption through body walls. For this **E.Fetida** is highly effective than other worms specially helps in the treatment of differential industrial waste water of dairy, Geltine, Palm oil mills, Coal producing industry and food industries .

Earthworms increase the hydraulic conductivity and natural aeration by granulating the clay particles. They also grind the silt and sand particles, increasing the total specific surface area, which enhances the ability to ‘adsorb’ the organics and inorganic from the wastewater. Intensification of soil processes and aeration by the earthworms enable the soil stabilization and filtration system to become effective and smaller in size. Suspended solids are trapped on top of the vermifilter and processed by earthworms and fed to the soil

microbes immobilized in the vermifilter. There is no sludge formation in the process which requires additional expenditure on landfill disposal. This is also an odor-free process and the resulting

vermifiltered water is clean and disinfected enough to be reused for farm irrigation and in parks and gardens. Hg Pollution can be evidenced by high level in soil, water and Biota.



Vermifiltration Technology working Principal

Method: - 3 different soils were spiked with 12 different concentration of inorganic mercury (Hg). Sub-chronic Hg toxicity tests were carried out with *Eisenia fetida* in spiked soils by exposing the worms for 28 days following standard procedure. The toxicity studied revealed that Hg exerted less lethal effect on earthworm in acidic soil with higher organic carbon (S-3 Soil) where water soluble. Hg fraction in soils with less organic carbon and higher Ph (S-1 & S-2 Soils). The concentration of Total Hg that caused 50% lethality to *E. Fetida* (Lc50) after 28 days of exposure in S-1, S-2 and S-3. Soils were 152, 294 and 367 mg kg⁻¹, respectively. The average weight loss of *E. Fetida* in 3 soil range from 5-65%. The worms showed less weight loss in the organic carbon-rich soil (S-3) compared to less organic carbon containing soils (S-1 and S-2). The Bio concentration of Hg in *E. Fetida* increased with increased Hg concentrations. The highest bioaccumulation took place in the acidic soil with higher organic carbon contents with estimated bioaccumulation factors. Ranging from 2 to 7.7. The finding of this study will be highly useful for deriving a more robust soil ecological guidelines value for Hg.

It is not possible to test and Monitor water quality at all places at all times, but there are ways to indirectly infer water quality using Bio indicators.

Laboratory Method:-

A laboratory methodology using the earthworm *Eisenia Fetida* was developed in this research to access mercury bioavailability in mine tailings and

aqueous solutions and examine. The influence of certain factors on mercury bio-availability in particular organic acids. The quick, inexpensive and simple earthworm protocol described here in was developed to priorities contaminated sites based on the potential for mercury. Incorporation into biota with specific consideration of the technical and financial limitation inherent in artisanal mining communities.

Methyl Mercury was about 3.01% of total mercury in Drawida sp. 12.02% of total mercury in *Alo.lobophera* sp. respectively. It suggested that mercury was mostly in inorganic forms in earthworms. Bioaccumulation factors of methyl mercury from soil to earthworm were much higher than those of total mercury, which suggested that methyl mercury might be more easily absorbed and accumulated in earthworms because of its Lipid solubility.

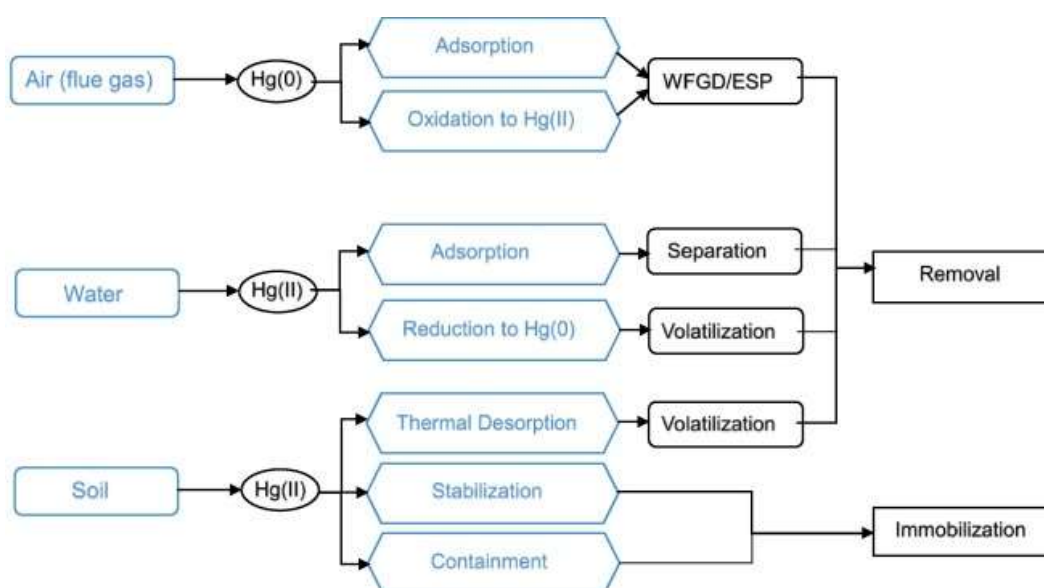
For soil improvement – Earthworm need the food and habitat provided by surface residue, and they eat the fungi that become more common in no till soils. As earthworm population increases, they pull more and more residue into their burrows, helping to mix organic matter into the soil, improving soil structure and water infiltration, nutrient cycling and plant growth. they are not only indicators of healthy soils system but their presence is usually an indicators of a healthy system.

Methylation of mercury in earth surface and the effect of mercury on the associated bacterial communities:-

Methylation compounds are very toxic for most organisms. Here we investigated the potential of earthworms to methylate inorganic Hg. We hypothesized that the anaerobic and nutrient-rich conditions in the digestive tracts of earthworms promote the methylation of Hg through the action of their gut bacteria. Earthworms were either grown in sterile soils treated with an inorganic (HgCl_2) or organic (CH_3HgCl) Hg concentration in the soils, earthworms and their casts were analyzed. The impact of Hg on the bacterial community compositions in earthworms was also studied. Tissue concentration of Methyl Hg in Earthworms grown in soil treated with inorganic-Hg were about

six times higher than in earthworms grown in soils without Hg concentrations. Methyl-Hg in the soils and earthworms casts remained at significantly lower levels suggesting that Hg was mainly methylated in the earthworms. Bacterial communities in earthworms were mostly restriction fragments (T-Rfs) affiliated to firmicutes were sensitive to inorganic and Methyl-Hg, whereas T-Rfs related to Betaproteobacteria were tolerant to the Hg treatments. Sulphate-reducing bacteria were detected in earthworms but not in soils.

Mechanisms involved in mercury remediation in Soil, water and Air:-



Adsorption and desorption for treatment of methyl Hg contaminated water:-

Among various methods aiming to remove $\text{Hg}(\text{II})$ from water solution, **fly ash adsorption** is the most commonly utilized approach (Fig. 2) (Abbas et al., 2018, Bao et al., 2017, Kyzas and Kostoglou, 2015, Rocha et al., 2016). The adsorbents usually possess high surface area as well as high porosity and the formation of chelates is the major sorption mechanism (Kyzas and Kostoglou, 2015, Rocha et al., 2016). Mondal et al. (2019b) synthesized **thioether-functionalized covalent triazine nanospheres** to adsorb Hg^{2+} and $\text{Hg}(0)$ from water. Excellent adsorption capability was observed (1253 and 813 mg/g for Hg^{2+} and $\text{Hg}(0)$, respectively), and the results of the kinetic study reveal a fast adsorption rate (9 times faster than that of TAPB-BMTTPA-COF and 7 times than PAF-1-SH). Another study by Abbas et al. (2018) synthesized a novel mesoporous conjugate adsorbent based on **pentasil zeolite (type ZSM-5)** to adsorb $\text{Hg}(\text{II})$ in aqueous solution, and the maximum adsorption capacity reached 172.6 mg/g. Bao et al.

(2017) utilized silica-coated magnetic nanoparticles to extract $\text{Hg}(\text{II})$ from wastewater, and the adsorption of mercury ions onto the imine (C-NH-) groups on the surface of nanoparticles was discovered. Another example used **chitosan derivatives as adsorbents**. The chelation between $\text{Hg}(\text{II})$ and the nitrogen atoms of chitosan is the dominant mechanism of adsorption (Kyzas and Kostoglou, 2015). The mechanism of adsorption is also commonly used for the removal of gas-phase elemental mercury [$\text{Hg}(0)$] (Abraham et al., 2018, Reddy et al., 2015). According to the “hard and soft acid-base” (HSAB) theory, Hg preferentially forms complexes with soft ligands such as sulfur to form insoluble and steady compounds (He et al., 2015). A high sulfur content of an adsorbent was found to promote the adsorption capacity for $\text{Hg}(0)$ (Abraham et al., 2018). While using adsorbents for Hg removal, it is of note that stability and reusability should be seriously considered, and more detailed discussion on this issue is provided in Section 3.

Oxidation & reduction Process for treatment of methyl Hg contaminated water treatment:-

Coal-fired power plants and coal producing company like **Carbon Continental** continued to be the predominant sources of anthropogenic mercury emission to the atmosphere (Bourtsalas and Themelis, 2019, Pirrone et al., 2010). **In typical coal combustion flue gas, mercury exist in three forms: elemental mercury [Hg(0)], divalent mercury [Hg(II)] and particulate bounded mercury [Hg(P)].** Among these forms, **elemental mercury** was recognized to be the hardest to be removed by conventional air pollution control devices owing to its volatility and low water solubility. The oxidation of Hg(0) has proven to be an effective way to decrease mercury emission (Chen et al., 2016, He et al., 2016, Krzyzyska et al., 2018, Liu and Wang, 2018). In most cases, Hg(0) was oxidized to Hg²⁺, which can be easily captured by an electrostatic precipitator (ESP) or wet flue gas desulfurization scrubbers (WFGD) due to its high solubility and sorption on particulate matter (Li et al., 2012, Liu et al., 2011, Qi et al., 2016, Wang et al., 2010a). Compared to the adsorption method (i.e. activated carbon injection, around 3–4 USD/kW)(Marczak et al., 2019), oxidation is more cost-effective. A number of studies have focused on a novel oxidation method, i.e., catalytic oxidation of elemental mercury from the flue gas, which will be elaborated in Section 4.3.1. Apart from the catalytic oxidation method, free radical advanced oxidation of Hg(0) is also utilized sometimes (Liu and Wang, 2018, Wang et al., 2010b, Wu et al., 2017a), but Hg(0) removal capacity using this technology remains limited thus far.

Reduction is often applied in order to prevent the formation of methylmercury (MeHg). Methylmercury is the most bioavailable form of mercury. Redox conditions in wetland sediments promote the formation of MeHg (Devai et al., 2005, Frohne et al., 2012, Lewis et al., 2016). A high concentration of Hg(II) species results in the production of MeHg. Therefore, an effective way to control methylmercury production is to decrease the concentration of Hg(II) (Benoit et al., 2001, Hsu-Kim et al., 2013). Zero-valent iron (ZVI) or Fe(II) are often employed to reduce Hg(II) to Hg(0), thus inhibiting MeHg production (Amirbahman et al., 2013, Lewis et al., 2016). Several studies also examined whether adsorbents could provide inhibition of MeHg production. A study by Muller and Brooks (2019) observed that **biochar** was ineffective at decreasing the total MeHg production in the aqueous phase. Another study by Zhang et al. (2019a) found that particulate-bound Hg(II) is crucial to methylation. In aquatic environments,

microbial methylation of particulate-bound Hg(II) should be considered.

Using Flyash as adsorbent for Treatment of Methyl Hg Contaminated Water:

Industrial waste is gaining much concern owing to the large amount of annual production. For example, coal fly ash (CFA) is a by-product of coal combustion of power plants, and the amount of its production is estimated to be 750 million tons worldwide (Attari et al., 2017, Yang et al., 2017a). Attari et al. (2017) **synthesized zeolite from CFA**, and the average efficiency of Hg²⁺ removal reached 94% with 10 mg/L initial concentration. Apart from CFA, red mud is a by-product of the Bayer Process for alumina production, and the global annual amount of production has reached 160 million tons (Yang et al., 2018b). After impregnation with potassium halides, modified red mud can be used for elemental mercury removal from flue gas. The halides (i.e. KI, KBr) promote the oxidation of captured Hg(0). Waste derived materials have significant potential for use in Hg remediation, but they may contain toxic metals and other contaminants (Bhattacharyya and Reddy, 2012, Hua et al., 2017), and further research should examine the potential risks associated with their application.

Apart from sulfur-rich minerals, other minerals, especially silicate minerals such as **zeolite, vermiculite and clay minerals can also be applied for mercury adsorption.** Although raw minerals show poor mercury adsorption capacity, chemically modified minerals have been reported to possess great adsorption abilities (Shao et al., 2016). Compared to other adsorbents such as activated carbon, this kind of material is a low-cost adsorbent, implying possible large-scale applications (Saleh et al., 2018). The major adsorption mechanism of clay minerals (i.e. montmorillonite, vermiculite and palygorskite) is ion exchange (Chen et al., 2015, Tran et al., 2015), while precipitation also plays a vital role in the case of Na-montmorillonite (Chen et al., 2015). Other minerals, such as zeolite and diatomite, possess a highly porous structure, which is beneficial for adsorption after functionalization with certain groups like hexadecyltrimethylammonium bromide (Shirzadi and Nezamzadeh-Ejhieh, 2017), CuBr₂ (Liu et al., 2019a) and thiosemicarbazones (Abbas et al., 2018). Removal efficacy of these porous materials depends largely on these groups, and minerals function as the supporting structure of the composite.

Biomass and industrial waste-derived materials methods for treatment of Methyl Hg Contaminated water

In recent years, waste-derived materials have received much attention for their cost-efficiency. Applying these materials to the remediation process is considered a more attractive and environmentally friendly method compared to landfill or incineration (Li et al., 2015c). In general, these materials can be divided into two categories according to the feedstock: industrial waste-derived materials and biomass-derived materials.

Biochar-based Hg removal for methyl Hg contaminated water:-

Eco-friendly biochars are regarded as promising adsorbents for mercury removal from water, and biochar based Hg removal is an innovative technology due to its excellent removal efficiency as well as cost-efficiency and environmentally friendliness (Boutsika et al., 2014, El Hanandeh et al., 2016, Faheem et al., 2018, Jia et al., 2019). The active sites on the surface of biochar such as —OH , C=O , π bond and C—O make it possible for chemical modification of biochar by adding thiol or amino groups with the aim of enhancing the adsorption capability (Huang et al., 2019b). Chemical binding of Hg^{2+} and surface active sites (e.g. —SH , —NH_2 , —OH , —COOH) is the major mechanism of adsorption (Huang et al., 2019b, Liu et al., 2016, Tang et al., 2015). It is noteworthy that biochars derived from different feedstocks may greatly influence the adsorption behavior, according to Liu et al. (2016). The results of X-ray absorption indicate that mercury binds to S in sulfur-rich biochars, and to O and Cl in biochars with low sulfur content. Feedstock will not only affect the binding mechanism of biochars, but also sulfate concentrations in the aqueous phase, which may restrict the utilization of certain types of biochars for mercury removal. This is because the raised SO_4^{2-} concentrations released from biochar (up to 1000 mg/L) can be used as electron acceptors, thus enhancing the activity of sulfate reducing bacteria, which are regarded as major Hg

methylators (Hsu-Kim et al., 2013). It has been reported that biochar produced from poultry manure or mushroom soil will elevate sulfate concentrations, so special care must be taken when selecting the feedstock of biochars to prevent the release of sulfate when treating mercury contaminated water (Liu et al., 2016). But results of Muller and Brooks (2019) indicate that SO_4^{2-} concentration (1–65 mg/L) did not influence Hg methylation. It is hypothesized that this discrepancy may be due to the variance of released SO_4^{2-} concentrations.

Biomass-derived materials include biochar and activated carbon derived from biomass (Table 4). Biochar is a black carbon derived from the pyrolysis of biomass. It is a novel porous material with high surface area, which is beneficial to mercury adsorption and immobilization (Beckers et al., 2019, O'Connor et al., 2018, Tang et al., 2015). The role of biochar in Hg remediation technologies will be discussed in 4.1.2 Immobilization with biochar and other amendments, 4.2.2 Biochar-based Hg removal, 4.3.4 Biochar-based flue gas treatment.

Activated carbon (AC) is an effective adsorbent removing various inorganic and organic contaminants from different media (e.g. wastewater or flue gas), but its high cost restricts large-scale use (approximately 135,000 USD/t) (Sajjadi et al., 2018). For instance, in flue gas treatment, the annual costs of activated carbon for a 250 MW boiler range from 796,000 to 2,562,000 USD/year, depending on the ESP type, and the annual costs of AC injection were estimated to be in the range of 420,674–20,225,000 USD/kgHg (EPPSA, 2015, Marczak et al., 2019). Generation of AC using waste feedstock therefore is promising. Kazemi et al. (2016) produced activated carbon through chemical activation of wood sawdust, and the surface area of AC reached 1789 m^2/g . Another study by Sajjadi et al. (2018) used pistachio wood waste to synthesize AC, with surface area and pore volume 1448 m^2/g and 0.901 cm^3/g , respectively.

Table A summary of feedstock and generation methods of various waste-derived materials utilized for mercury remediation.

Material	Feedstock	Generation method	Treated mercury species (target media)	Reference
Zeolite Linde Type A	Coal fly ash	Microwave irradiation	Hg^{2+} (W)	(Attari et al., 2017)
Bioelastomeric foam	Coffee waste	Sugar leaching	Hg^{2+} (W)	(Chavan et al., 2016)
Drinking water treatment residuals	—	—	HgCl_2 (S)	(Deliz Quiñones et al., 2016)

Material	Feedstock	Generation method	Treated mercury species (target media)	Reference
Drinking water treatment residuals	–	–	Hg(OH) ₂ (S)	(Elkhatib et al., 2017)
Biochar	Pine sawdust	Pyrolysis	Hg ²⁺ , CH ₃ Hg ⁺ (W)	(Huang et al., 2019b)
Activated carbon	Fir wood sawdust	Chemical activation	Hg ²⁺ (W)	(Kazemi et al., 2016)
Biochar	Medicine residue	Pyrolysis	Hg(0) (G)	(Li et al., 2015b)
Char	Waste tire	Pyrolysis	Hg(0) (G)	(Li et al., 2015c)
Activated carbon	Wood waste	Chemical activation	Hg ²⁺ (W)	(Sajjadi et al., 2018)
Coal fly ash	–	–	Hg(0) (G)	(Yang et al., 2017a)

Immobilization Hg in Soil with biochar and other amendments

A few studies investigated the effect of biochars on immobilizing Hg in soil (Table 6). For instance, a fully-crossed small plot study by Gilmour et al. (2018) applied pine dust biochar in immobilizing MeHg in a salt marsh, and found that the application of biochar did not reduce total Hg, and that the removal efficiency of MeHg was not satisfactory. However, the application of sulfur-modified biochar proved to be an ideal approach to reducing Hg²⁺ in contaminated soil (O'Connor et al., 2018). Rice husk was modified with non-toxic elemental S, which increased the biochar's Hg²⁺ adsorptive capacity by 73%, to 67 mg/g, and the treatment dosage of 5% (dry wt.) reduced 99.3% of freely available mercury in TCLP leachates compared to untreated soil

(O'Connor et al., 2018). Apart from biochar, other immobilization amendments were also utilized for the remediation of methylmercury, such as activated carbon (Gilmour et al., 2018) and activated clay (Yin et al., 2016). When it comes to the immobilization of Hg(0), selenium nanoparticles turned out to be effective (Wang et al., 2019c, Wang et al., 2017b). Under aerobic and anaerobic conditions, selenium nanoparticles converted 45.8–57.1% and 39.1–48.6% of the Hg(0) in the soil to the insoluble mercuric selenide (HgSe), respectively (Wang et al., 2017b). The addition of biochar and other immobilization amendments is innovative, and mechanisms of Hg-immobilization are still not fully understood. In addition, we argue that field studies be conducted to examine the feasibility of these immobilization amendments in real occurrences.

Table A list of production parameters and properties of biochar used for Hg removal in different media.

Feedstock	Pyrolysis temperature (°C)	Heating rate (°C/min)	Residence time (min)	Surface area (m ² /g)	Pore volume (mL/g)	Treated media	Reference
pine cone	200, 500	7	120	192.97	10.2	soil	(Beckers et al., 2019)
pine sawdust	500	10	120	44	0.051	soil	(Chen et al., 2018b)
rice husk	550	15	120	143	0.042	soil	(O'Connor et al., 2018)
pine sawdust	700	10	180	335.40	0.152	water	(Huang et al., 2019b)

Feedstock	Pyrolysis temperature (°C)	Heating rate (°C/min)	Residence time (min)	Surface area (m ² /g)	Pore volume (mL/g)	Treated media	Reference
pine sawdust	500	10	180	52.25	0.026	water	(Huang et al., 2019b)
wheat straw	600	n.a.	60	4.5	0.0092	water	(Tang et al., 2015)
pine sawdust	400	5	60	80.35	0.18	water	(Wang et al., 2018a)
cotton straw	600	n.a.	60	203.7	0.162	flue gas	(Li et al., 2015d)
municipal solid waste	600	n.a.	120	12.4	0.040	flue gas	(Li et al., 2015a)
herb medicine residue	600	20	60	24.92	0.0375	flue gas	(Li et al., 2015b)
seaweed	800	20	20	26.20	0.034	flue gas	(Liu et al., 2018b)
herb medicine residue	600	20	60	24.9	0.0375	flue gas	(Shen et al., 2015)
waste tea	500	n.a.	120	142.05	0.086	flue gas	(Shen et al., 2017)
tobacco straw	600	10	60	8.2	n.a.	flue gas	(Wang et al., 2018b)
rice straw	600	n.a.	20	26.66	0.121	flue gas	(Xu et al., 2018)
seaweed	800	n.a.	20	21.15	0.466	flue gas	(Xu et al., 2019)
wheat straw	600	n.a.	20	65.151	0.184	flue gas	(Yang et al., 2017b)

Microbial reduction and volatilization for treatment of methyl Hg Contaminated water :-

Because Hg²⁺ in soil could be converted to the most toxic form methylmercury, reducing Hg²⁺ to elemental mercury Hg(0) is considered to be detoxification (Wagner-Dobler, 2003). Mercury resistant bacteria are used in this microbial reduction and volatilization process, because they possess the *mer* operon (Nascimento and Chartone-Souza, 2003). The *mer* operon carries a number of genes and gene products closely related to the mercury tolerance and reduction mechanism of these bacteria (Mahbub et al., 2016, Mahbub et al., 2017, Mathema et al., 2011, McCarthy et al., 2017). As is shown in Fig. 3, *merP* and *merT* genes express transporter proteins which enable Hg to enter the

cytoplasm. Then the mercuric reductase enzyme encoded by *merA* reduces Hg²⁺ to Hg(0), which diffuses passively out of the cell (Chen et al., 2018d, Quinones et al., 2013). In some bacteria *merB* gene expresses organomercury lyase enzyme, which can break the C—Hg bound in organic compounds, making the mercury ion available for the reduction (Barkay et al., 2003). Mahbub et al. (2016) used a highly Hg resistant strain *Sphingobium* SA2 for reduction and volatilization of mercury, and 79% of mercury was volatilized in 6 h. Another research conducted by Mahbub et al. (2017) found 44% removal rate within 6 h dominated by *Sphingopyxis* sp. SE2. In order to improve the bioavailability of mercury, Chen et al. (2018d) utilized a chemical

extraction procedure before bacteria reduction. Ten hours of ammonium thiosulfate (0.5 M) extraction was used to extract mercury from the soil to the water phase. Then reduction of Hg^{2+} was conducted and the removal rate reached 81%. Compared to a one-stage method that only involves bacterial

reduction and volatilization, the two-stage approach is not a cost-effective and green method for remediation. How to increase the removal rate of mercury using simpler methods deserves further investigation.

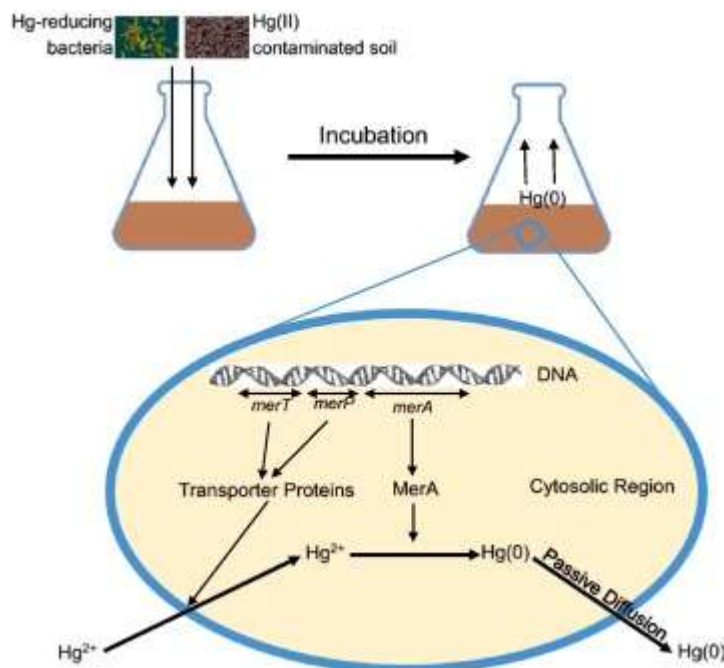


Fig. A conceptual figure for microbial reduction and volatilization of mercury. MerA: the mercuric reductase enzyme encoded by *merA* gene.

Algae-based methyl Hg removal from contaminated water:-

The application of marine macroalgae is a cost-effective technology for mercury removal from saline waters (Henriques et al., 2015). Marine algae can be divided into three categories: brown algae (Phaeophyta), red algae (Rhodophyta) and green algae (Chlorophyta), the differences of which lie in the cell wall, indicating binding preferences for different metals (Romera et al., 2007). A study by Henriques et al. (2015) investigated the Hg^{2+} removal efficiency of three types of algae, and found that *Ulva lactuca*, a green macroalgae which possesses several functional groups such as hydroxyl, amino, sulfate and carbonyl, performed best. Mercury removal is attributed to both bioaccumulation by the living organisms and biosorption on the biomass, either from living or non-living algae. Compared to bioaccumulation, biosorption by dried biomass is a much quicker process, because only physicochemical mechanisms account for the Hg adsorption. However, the utilization of living macroalgae showed better removal efficiency, because the adsorbed mercury was transported into the cells, freeing the binding sites for subsequent adsorption (Henriques et al.,

2015). Upon accumulation, Hg will bind strongly in macroalgae tissues without being transferred to more toxic species such as methylmercury, which was also found in another study (Henriques et al., 2017). In both studies, the bioconcentration factor of mercury was as high as 2000 (Henriques et al., 2017, Henriques et al., 2015), indicating great mercury accumulation ability of *Ulva lactuca*. However, discrepancy exists whether Hg will not be transferred into MeHg by algae. Lei et al. (2019) found that algal organic matter enhanced the abundance of microbial methylators, thus raising MeHg concentrations in a eutrophic lake. This discrepancy may be due to the algal species, and deserves further investigations. Besides, this technique can only be applied when the initial concentration of Hg^{2+} exerts no critical toxic effect to cells (both studies adopted an initial concentration of $100 \mu\text{g/L}$), which has limited its application.

Challenges and future research directions

Traditional remediation technologies have been applied widely for mercury removal, despite some significant disadvantages. Firstly, the high cost of some methods such as thermal desorption and

adsorption by activated carbon is an obstacle for large-scale applications (Gilmour et al., 2018, Ma et al., 2015). When it comes to mercury stabilization and containment in soil using technologies that are suited for application on large sites, long-term monitoring of the stability of mercury should be conducted (Wang et al., 2012).

The major mechanism for Hg removal by emerging remediation materials is adsorption.

Various materials with high specific area, large porosity and active sites for mercury are explored in numerous studies. Although features such as specific area, pore size and adsorption capacity have been thoroughly investigated to reveal the characteristics of sorbents, it is suggested that future research focus on the partition coefficient of Hg species to compare the adsorption efficiency of different materials easily. In addition, more studies should be conducted to examine the adsorption efficacy of these sorbents in environmentally relevant solutions, as solution chemistry affects their adsorption performance greatly. For instance, dissolved organic matter (DOM) strongly affects Hg speciation, transformation and reactivity in natural waters. The complexation of Hg(II)-DOM can make Hg(II) unavailable for adsorption (Johs et al., 2019). Under sulfidic conditions, microbial methylation can be enhanced owing to the increased bioavailability of Hg(II) (Graham et al., 2012). Besides, other co-existing metal ions may cause competitive adsorption, thus affecting the adsorption performance (Leus et al., 2017). In order to reduce the cost, waste-derived materials are utilized for mercury adsorption. However, other toxic constituents may exist in these materials, causing potential health risks. Another pathway to maximize cost-efficiency of emerging materials is reuse. Some studies have investigated the regeneration of adsorbents, and most of the emerging materials showed great potential for reuse, while other materials like MOFs and minerals cannot be regenerated while maintaining their sorption capacity (Ke et al., 2017).

Some innovative remediation technologies such as **microbial reduction and photocatalytic nano-**array lack large-scale applications, and the effectiveness of these innovative technologies in field conditions should be examined. Remediation methods involving the transformation of mercury by organisms such as phytoremediation and algae-based Hg removal can only be utilized when Hg concentrations do not exert toxic effect on organisms. Besides, the removal efficiency of mercury from the flue gas is affected by other components in the flue gas (e.g. SO₂, NO_x and H₂O). After Hg(0) oxidation, how to properly handle the

oxidized Hg(II) in the fly ash is another problem. The fly ash should be stabilized to avoid Hg leaching, and feasibility of fly ash utilization for other purposes should be assessed carefully. For these innovative methods to be validated, future studies should consider following aspects: (1) the translation of experimental data to full scale operation, i.e., the industrial scale or field conditions in the case of soil remediation; (2) the combination of different remediation technologies such as combination of phytoremediation and microbial reduction to create genetically modified plants which can reduce Hg²⁺ to less toxic Hg(0); (3) improving the separation efficiency of the adsorbents from environmental media, especially from water; (4) methods for simultaneous detection and removal of mercury from aqueous phase; (5) diminishing the impact of other constituents in the flue gas during the adsorption and oxidation process of elemental mercury.

Future Prospects :-

More recent research have been ongoing to develop novel materials and technologies for Hg remediation (Ali et al., 2018, Chen et al., 2018c, Huang et al., 2019b, Moharem et al., 2019, Wang et al., 2019b, Xu et al., 2019). Novel materials, especially materials possessing high surface area, large porosity as well as active sites for adsorption, have been examined extensively in recent studies (Gusain et al., 2019, Kumar et al., 2019). Apart from adsorption capacity which is the key determinant of these materials, other issues such as generation method, stability and reusability should be seriously considered as well (Abraham et al., 2018, Ke et al., 2017, Ram and Chauhan, 2018, Tack et al., 2019). Compared to conventional remediation technologies such as thermal desorption or activated carbon adsorption, innovative methods have proved to be more cost-efficient and environmentally friendly. Interestingly, most of these technologies treating Hg contaminated soil, water and air can either be based on emerging materials or the metabolism of organisms, namely plants, algae and bacteria. The aim of this work is to review current knowledge on emerging materials as well as innovative technologies for mercury remediation in soil, water and air. This review discusses the synthesis method, morphology, adsorption behavior, reusability, stability as well as other characteristics of emerging materials. The review also focuses on the remediation mechanisms and remediation efficacy of novel technologies and proposes critical future research directions in this field.

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