RIVER WATER MERCURY CONTENT ANALYSIS AT PALAKKAD DISTRICT AND THE DESIGN OF MERCURY ADSORBING CFL DISPOSAL SYSTEM

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Abstract -*Analysis of mercury content has been conducted by taking samples from tributaries and sub tributaries of Bharathapuzha river at Palakkad district. Subsurface and bottom sediment samples were taken. Temperature and pH of the samples were also noted. The analysis was conducted at Sophisticated Test and Instrumentation Centre lab at Ernakulam. The instrument used for the analysis was Hydra C direct mercury analyzer which works on the principle of thermal decomposition with Atomic Absorption Spectroscopy. The analysis results showed that there was no presence of elemental mercury in all the subsurface samples. But in the analysis of two sediment samples it was found that the elemental mercury was 0.02mg/l. When mercury reacts with water methylation of mercury will occur, thus forming methyl mercury, which is the main cause of the Minamata disease. CFLs play an important role in the contamination of river, as it contains 3-5 mg of mercury per CFL. As a solution for the contamination of rivers through mercury from CFLs a mercury adsorbing CFL disposal system was designed, in which the mercury in the CFLs are converted into HgO by using a compound made up of titanium dioxide, sulphur and acetic acid. Chemical experiments were conducted with (1) Titanium dioxide (2) Titanium dioxide and Acetic acid (3) Titanium dioxide, Sulphur and Acetic acid. All the experiments were conducted under the presence of sunlight, as the titanium dioxide is a photocatalyst. Results showed that the compound made up of Titanium dioxide, Sulphur and Acetic acid reacts faster with the mercury content in the CFL under the presence of UV light from the sun. The HgO formed is collected and the CFL glass can be given to glass factories for recycling.**

Key Words: *Methyl Mercury,River, Sulphur, Titanium Dioxide*

1. INTRODUCTION

Mercury is a very toxic element which can be found both as an introduced contaminant and naturally in the environment. Its high potential for toxicity was well documented in the highly contaminated areas of Minamata Bay, Japan in the 1950's and 1960's. Mercury can be a menace to people's health and wildlife in many environments that are not discernibly polluted. The risk is determined by the form of mercury present, the likelihood of exposure and the ecological and geochemical factors that influence how mercury moves and changes form in the environment. Mercury's toxic effects depends on the route of exposure and its chemical form. The most toxic form of mercury is methylmercury [CH_3Hg]. It affects the immune system, alters enzyme and genetic systems, and damages the nervous system, including the senses of taste, touch, sight and coordination. Developing embryos are particularly damaged by methyl mercury, which are very much sensitive than adults. Ingestion is the main path of exposure to methylmercury, and it is more rapidly absorbed and more slowly excreted than other forms of mercury.Mercury in its normal state is not dangerous, but when it reacts with water it becomes the deadly poisonous methyl mercury which is the main cause of Minamata disease. Studies regarding the mercury pollution in river water are still undergoing, and in Palakkad District, Kerala no serious studies regarding the mercury pollution in river water has conducted yet and also there is no mercury tracing instrument in the Kalmandapam laboratory for the detection of mercury in the water samples. This motivated me for conducting an analysis for the determination of mercury in river water at Palakkad district. The testing and analysis of water samples was done at STIC (Sophisticated Test and Instrumentation Centre) Lab, Kalamassery, Kerala as they are having mercury tracing instrument. A new mercury adsorbing CFL disposal system is also designed inorder to reduce the mercury emission to environment.

2. SAMPLE COLLECTION

Samples were taken from tributaries and sub tributaries of Bharathapuzha river.The major rivers of Palakkad and their tributaries are given below. After the Periyar river, Bharathapuzha is the second-longest river in Kerala.

Samples were taken from tributaries and sub-tributaries of Bharathapuzha river.

- Bharathapuzha: The river takes its origin from Anamalai hills and flows through the districts of Palakkad, Thrissur and Malappuram before emptying into the Arabian sea at Ponnani. Its four main tributaries are Thuthapuzha, Kalpathypuzha, Kannadipuzha and Gayatripuzha
- Gayathripuzha: Anamalai hills is the origin of Gayathripuzha and after traversing through Nenmara, Kollengode, Alathur, Pazhayannur and Vadakkanchery joins Bharathappuzha at Mayannur. Ayalurpuzha, Mangalam river, Meenkarapuzha, Vandazhipuzha and Chulliyar are the five main sub-tributaries of this river.
- Kannadipuzha: It is also known as Amaravathipuzha or Chitturpuzha. This river, which also starts from the Anamalai hills, flows through Tattamangalam and Chittur and joins the main river at Parli. Aliyar,Palar and Uppar are the three main streams combine to form this river.
- Kalpathypuzha:This river starts from the place called Chenthamarakulam in the hills, north of Walayar. Korayar, Walayar, Varattar and Malampuzha are the four streams which forms the river Kalpathypuzha.
- Thuthapuzha: This river starts from the Silent Valley hills and joins the main river about two kilometers off Pallippuram railway station. Ambanakkadavu, Kunthipuzha, Thuppanadippuzha and Kanjirapuzha are the important streams which feed this tributary.

2. MATERIALS AND METHODS

The method used for the sampling of water was EPA 1669 and that used for analysis was EPA 7473 and the instrument used for the analysis of mercury was Hydra C direct mercury analyzer.

2.1 EPA Method 1669

- All sample containers and sampling equipments are cleaned in a cleaning facility or laboratory using mineral acids, reagent water and detergent before samples are collected.
- Sample containers after cleaning are filled with weak acid solution, double bagged individually, and shipped to the sampling site.
- "Dirty hands" is designated to one member of the two-person sampling team; and "clean hands" is designated to the second member upon arrival at the sampling site. "Clean hands" handle all operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle. Operation of the machinery, preparation of the sampler (except the sample container itself) and for all other activities that do not involve direct contact with the sample is done by "dirty hands".
- All sample containers and sample equipments used for metals determinations must be nonmetallic and free from any material that may contain metals.
- Sampling personnel are required to wear clean, non-talc gloves at all times when handling sample containers and sampling equipments.
- A field duplicate must be collected at each sampling site, in addition to processing field blanks at each site or one field duplicate per every 10 samples, whichever is more frequent.

2.2 EPA Method 7473

EPA 7473 involves the mercury detection in solution and solid samples by thermal decomposition, amalgamation and atomic absorption spectrophotometry. Thermal decomposition is the complete or partial degradation of samples using conduction and convection heating mechanisms resulting in the release of volatile components such as carbon dioxide, water, organic substances,elements in the form of complex compounds or oxides, and elemental gases. The process by which mercury forms a metal alloy with gold is called amalgamation. Atomic absorption spectrometry (AAS) is technique that measures the concentrations of elements analytically. Atomic absorption is very sensitive. In a sample, it can measure down to parts per billion of a gram. The AAS technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to higher energy level. Thermal decomposition sample preparation along with atomic absorption detection reduces the total analysis time of most samples to less than 5 min in either field setting or in the laboratory. Without sample chemical pre-treatment, both organic and inorganic mercury in sediments, soils, bottom deposits and sludge-type materials as well as in ground waters and aqueous wastes can be determined using this method. Liberation of mercury from aqueous samples and solids in the instrument is done by controlled heating in an oxygenated decomposition furnace. The sample is dried and then thermally and chemically decomposed within the decomposition furnace. The flowing oxygen carries the decomposition products to the catalytic section of the furnace. Oxidation is completed and sulphur/nitrogen oxides and halogens are trapped. The remaining decomposition products are then carried to an amalgamator that selectively traps mercury. To remove any remaining gases or decomposition products, the system is flushed with oxygen. After flushing, the releasing of mercury vapor will occur when the amalgamator is rapidly heated. The mercury vapor is carried with the flowing oxygen through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. As a function of mercury concentration absorbance is measured at 253.7nm.

2.3 Hydra-C Mercury Analyzer

Hydra-C operates on the principle of thermal decomposition to liberate elemental mercury from solid or liquid samples. Fig-1 shows Hydra-C direct mercury analyser.

Fig -1: Hydra-C Direct Mercury Analyzer

Fig-2 shows the principle of operation of Hydra-C mercury analyser. First, in a sample boat, a weighed sample is deposited and introduced into the decomposition furnace. An oxidant (typically compressed air or oxygen) begins to flow over the sample, after the furnace is closed and the furnace temperature is increased in two stages; first for drying the sample, then to decompose it.

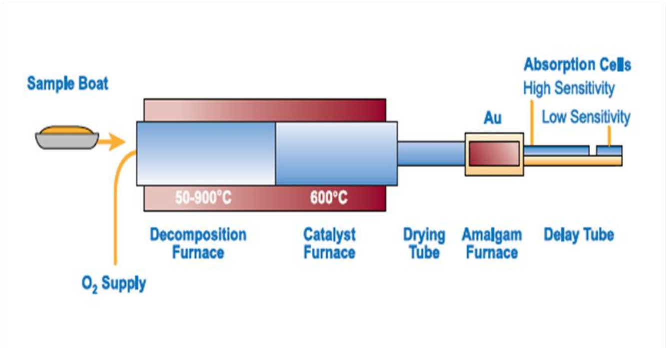

Fig -2: Principle of Operation of Hydra-C

Thermal decomposition of the sample at high temperatures with oxygen is the analytical process typically involving; although, gentle heating of the sample in air is adequate to release the mercury for some applications. During the combustion step the evolved gases are carried through a heated catalyst to produce free mercury while removing nitrogen oxides, sulphur oxides and halogens. Through a dryer the remaining combustion products including elemental mercury (Hg) are swept first and all the elemental mercury is captured through a gold amalgamation trap. Following the decomposition step, the amalgamation trap is heated and the free mercury is carried into an atomic absorption spectrometer.

3. ANALYSIS RESULTS

Samples were taken from different locations of tributaries and sub-tributaries of Bharathapuzha river. Subsamples and sediment samples were taken. 39 samples were taken from tributaries and sub-tributaries of Bharathapuzha river.

Table -1: Analysis Results

No	River	Surface	pH	T (˚C)	DL (ng/g)	Con (ng/g)
1	Bharathapuzha	Sub	7.9	32.3	1	BDL
2	Bharathapuzha	Sub	7.9	32.3	1	BDL
3	Bharathapuzha	Sub	8	33	1	BDL
4	Bharathapuzha	Sub	7.7	30.9	1	BDL
5	Bharathapuzha	Sub	7.9	27.3	1	BDL
6	Bharathapuzha	Sub	7.9	29.3	1	BDL
7	Nellipuzha	Sub	8.2	30	1	BDL
8	Nellipuzha	Sub	8.9	34.5	1	BDL
9	Nellipuzha	Sub	8.3	32	1	BDL
10	Gayatripuzha	Sub	8.2	30.5	1	BDL
11	Mangalam	Sub	7.4	32.9	1	BDL
12	Ayaloorpuzha	Sub	7.9	29.6	1	BDL
13	Vandazhipuzha	Sub	8.3	30	1	BDL
14	Chulliyar	Sub	8.2	29.8	1	BDL
15	Chitturpuzha	Sub	8.7	31.4	1	BDL
16	Korayar	Sub	7.7	28.7	1	BDL
17	Varattar	Sub	8.5	28.3	1	BDL
18	Walayar	Sub	8.5	29.6	1	BDL
19	Walayar	Sub	8.5	29.6	1	BDL
20	Thoothapuzha	Sediment	8.3	24	10	BDL
21	Korayar	Sediment	8.4	25	10	20
22	Kalpathypuzha	Sediment	8.6	26.2	10	20
23	Varattar	Sediment	8.2	25.2	10	BDL
24	Walayar	Sediment	8.1	25.6	10	BDL
25	Kunthipuzha	Sediment	7.9	24	10	BDL
26	Nellipuzha	Sediment	7.8	24.2	10	BDL
27	Gayatripuzha	Sediment	7.6	25.5	10	BDL
28	Mangalam	Sediment	8.2	26.8	10	BDL
29	Kanjirapuzha	Sediment	8.3	23.2	10	BDL
30	Chulliyar	Sediment	8.2	24.4	10	BDL
31	Ayalurpuzha	Sediment	8.4	24.6	10	BDL
32	Bharathapuzha	Sediment	8.2	25.2	10	BDL
33	Bharathapuzha	Sediment	8.1	24.8	10	BDL
34	Bharathapuzha	Sediment	7.6	24.1	10	BDL
35	Bharathapuzha	Sediment	8.2	25.3	10	BDL
36	Bharathapuzha	Sediment	8.1	25.2	10	BDL
37	Bharathapuzha	Sediment	7.9	24.3	10	BDL
38	Vandazhipuzha	Sediment	7.8	27	10	BDL

pH and temperature of surface were noted for each sample by using a pH meter along with a temperature gauge. pH of all samples were in between 7 and 8.5 and the temperature range was in between 24-35 degree Celsius. Samples were taken in the months of March, April and May.

The samples were taken to the STIC lab for analysis purpose. The detection limit of subsurface samples was 1ng/g and that of sediment samples was 10ng/g. Analysis results showed that there is no trace of mercury in all the subsurface samples. But the amount of elemental mercury in two of the sediment samples which were taken from Korayar river and Kalpathypuzha river was found to be 0.02mg/l which is greater than the maximum permissible limit of 0.01mg/l. The analysis results are shown in Table.I.Analysis results showed that the amount of elemental mercury is higher in concentration at Korayar river and Kalpathypuzha river and it is 0.02mg/l.

3. ADSORPTION OF MERCURY

Titanium dioxide in its anatase form is an excellent adsorbent for the adsorption of mercury in vapour phase. Mercury in CFL can be either in vapour form or in elemental form. Elemental form mercury can be converted into metacinnabar (HgS) by using sulphur as the sorbent, but it is not effective for vapour phase mercury sorption. Chemical experiments were conducted on mercury with (a) Titanium dioxide (b) Titanium dioxide and acetic acid and (c) Titanium dioxide, sulphur and acetic acid. Experiments were conducted under the presence of sunlight as the titanium dioxide is a photocatalyst.

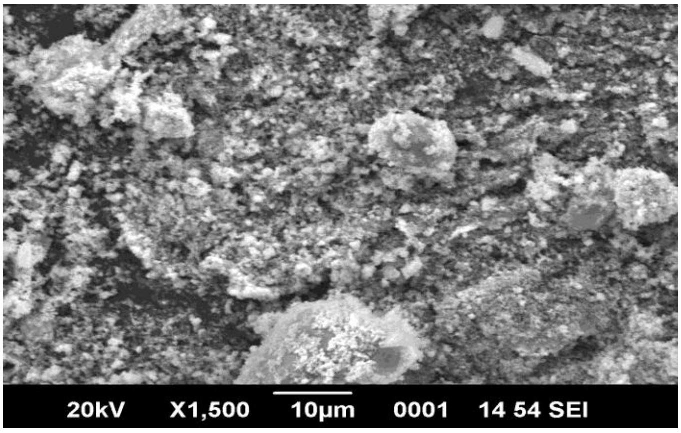

Fig -3: SEM Image of HgO formed by the reaction of Mercury with Titanium Dioxide, Sulphur and Acetic Acid

Titanium dioxide mixed with sulphur makes photocatalytic activity faster. Experiment results showed that the compound made up of titanium dioxide, sulphur and acetic acid with mercury showed fast reaction to form HgO. The compound thus formed has given for SEM imaging. Acetic acid (CH_3COOH) is used as the dispersing agent inorder to fast up the reaction process. The elemental form mercury can be easily scattered by using acetic acid. Fig-3 shows the Scanning Electron Microscopic (SEM) image of HgO formed by the reaction of mercury with titanium dioxide, sulphur and acetic acid. SEM imaging was also done at STIC lab. SEM imaging was done in the Secondary Electron Imaging (SEI) mode. The secondary electrons are electrons generated as ionization products. They are called 'secondary' because they are generated by the primary radiation. This radiation can be in the form of electrons, photons or ions with sufficiently high energy, i.e. exceeding the ionization potential. Secondary electron detectors are common in all SEMs. A SEM with secondary electron imaging or SEI can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size.

3. DESIGN OF CFL DISPOSAL SYSTEM

This CFL disposal system consists of two inlets, a solution chamber, a control valve, a motor of 750 Watts, blade mechanism and a collecting chamber. Fig-4 shows the side view of CFL disposal system. The working of this system is as follows. The CFL is inserted through the first inlet to the solution chamber where the chemical solution which is made up of titanium dioxide, sulphur and acetic acid has been deposited. The CFL is slightly twisted so that the CFL gets break up within the solution itself. Now the glass portion of the CFL is coated with this solution and it is taken back and it is placed in the second inlet.

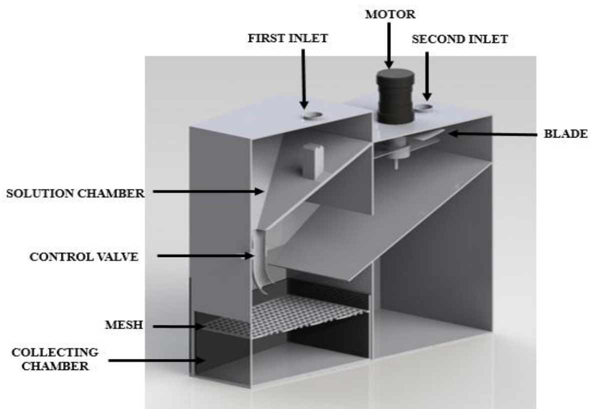

Fig-4: Side View of CFL Disposal System

There is a blade placed inside the second inlet which is powered by a 750 W motor. At this time the glass portion of the CFL is completely broken and it is passed to the collecting mesh. This system is designed for 50 CFLs. So after depositing 50 CFLs the control valve is opened so that the solution along with the remaining glass pieces will come down and the glass pieces gets deposited on the mesh and the solution will goes to the collecting chamber. The solution thus collected is given back to the solution chamber and the mesh along with the glass pieces is taken out and is placed under the presence of sunlight till the solution gets dried up and forms the HgO which is black in colour.

3. RESULT AND DISCUSSIONS

A new CFL disposal system has been designed in which the elemental or vapour phase mercury is converted into HgO. This HgO formed is collected and the glass portion of the CFLs is given to the glass factories for recycling.

4. CONCLUSION

As a solution for the contamination of rivers due to the release of mercury by the unscientific disposal of CFLs, a new CFL disposal system along with mercury adsorption is designed, in which the mercury in the CFL is converted into HgO by the photocatalytic reaction of titanium dioxide. By the implementation of this system, the mercury pollution to the environment can be considerably reduced, thus ensuring the safety of human beings and wildlife.

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BIOGRAPHIES

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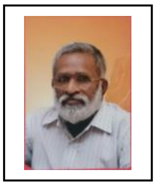

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