

Removal of Mercury in Thermal Plant Waste Water Discharge

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Abstract—Mercury is a toxic metal that causes harmful effects to living organisms and the environment. Coal-fired power plants are the major sources of mercury emission around the world and also in India. Globally, mitigation of mercury emission is gaining attention. Wastewater disposal in ash ponds is widely practiced for the disposal of the wastes generated in power plants which highly contaminate the surroundings with the heavy metal. Membrane technology can be exploited for the removal of trace level concentration of mercury present in these wastewaters. In this study, use of tri n-butyl phosphate (TBP) based supported liquid membrane (SLM) has been investigated for the removal studies of the wastewater sample. Concentration of mercury was determined using Cold vapour atomic fluorescence spectrophotometer (CVAFS) and the removal efficiency was calculated. The initial concentration of mercury in wastewater was obtained to be 18 ppb. SLM reactor was able to remove almost all the mercury ions within ten minutes of reaction time. The current study demonstrated the ability of TBP based SLM reactor to be utilized for mercury removal studies.

1. INTRODUCTION

All forms of mercury, namely, elemental, organic and inorganic are toxic to living organisms even in traces [5]. Mainly, presence of mercury in water affects the aquatic species and thereby entering into the human ecosystem (NESCAUM 2003). Acute exposure to mercury causes deleterious effects in humans, affecting the central nervous system, lungs and kidneys [10]. As per the U.S. Environmental protection agency, the water quality standard for the discharge of mercury in wastewater is set to be 0.005 ppm.

Anthropogenic emission of mercury is predominantly contributed from the energy sector, especially from the coal combustion process used in thermal power plants [8]. India is highly dependent on the coal fired power plants for energy production and is the third largest producer of coal in the world [11]. Mercury is found to be in rich quantities in Indian coal. The average concentration of mercury is observed to be in the range of 0.01 to 1.1 ppm [4]. In future, mercury emissions are supposed to increase owing to the raising energy demands (NESCAUM 2003).

About 87% of the country's mercury emission is contributed from the coal-fired power plants [11]. The dissipative nature

of mercury makes it an important pollutant that initiates careful examination and thereby, management. At the vicinity of power plants, contamination of air, water and soil is unavoidable as the metal is of monoatomic nature with low melting and boiling points [4]. Thus, a comprehensive approach of incorporating measures to reduce the emissions from the power plants is the need of the hour (NESCAUM 2003).

The various ways in which mercury is emitted from the coal-fired power plant include elemental gaseous vapour, oxidised form and in condensed form on particles. Both elemental and oxidised forms of mercury can undergo chemical reactions easily and be converted to methylmercury which is highly toxic in nature [6]. Both organic and inorganic forms of mercury are discharged in coal fly ash, bottom ash and boiler slag. Among these, coal fly ash contains more than 50% of mercury emitted from power plants. Ash ponds are widely used in power plants for the disposal of both coal fly ash and bottom ash wastes [3]. The major problem with this mode of disposal is the potential leaching of the toxic metals to soil, surface water and ground water [9]. Selective separation of mercury from the wastewater can be achieved using membrane technology [12].

SLM has been widely used for the removal of heavy metals in trace concentrations [12]. SLM comprises of a polymeric support immersed in an organic carrier that separates the two solutions. Studies have been reported for the removal of mercury from synthetic solutions using various carriers [2]. TBP is an emerging carrier for the removal studies as it has high extraction capacity, less solubility, high flash point and low cost [13]. Hence, there exists a scope for the application of TBP based SLM for the removal of mercury from the wastewater generated in coal-fired power plant.

In this study, removal of mercury ions from the wastewater collected from a power plant has been attempted using SLM reactor. The aim is to determine the removal efficiency of the TBP based SLM reactor in separating mercury ions from the wastewater.

2. MATERIALS AND METHODS

Collection of wastewater samples

Wastewater samples were collected from the ash pond of a thermal power plant, situated in Chennai. Samples were collected in a Teflon bottle which was pre-cleaned with nitric acid and distilled water. pH and conductivity of the samples were measured and then acidified with 2% of Hydrochloric acid. The samples were filtered through 0.45 μ filter paper and stored at 5°C.

Characterization of wastewater samples

pH of the wastewater sample was obtained using Elico pH meter (model: Li 120). The sample was subjected to identification of the various heavy metals that were in trace concentrations. Inductively coupled plasma optical emission spectroscopy (ICP-OES) (Model: iCAP 6500, thermo scientific) was used for the determination of heavy metals. Mercury concentration was determined using CVAFS.

SLM reactor studies

Polytetrafluoroethylene membrane (thickness: 58 μ m, pore size: 0.45 μ m, porosity: 75 %, effective contact area: 13.2 cm²) was used to prepare SLM with 90 % and 10% composition of TBP and hexane, respectively. SLM reactor is made up of glass with a teflon holder in the middle to support the polymeric sheet as shown in Figure 1. Feed and strip phase solutions were taken on either sides of the membrane and stirring effect was also provided to the reactor. Wastewater sample (150 ml) was taken in the feed side and 0.4 M NaOH (150 ml) solution was taken in the strip side of the reactor and the prepared SLM was placed as an interface. Stirring rate of the magnetic stirrer was maintained at 300 rpm.

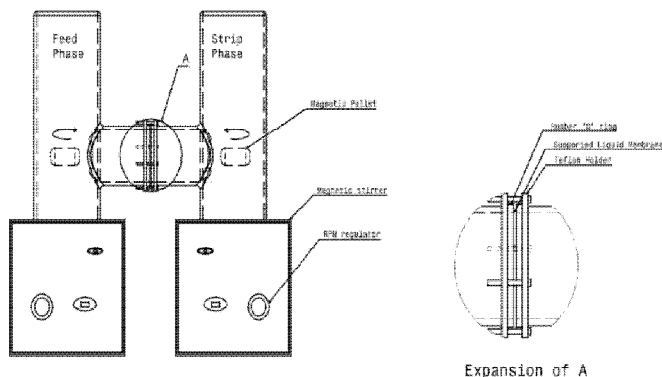


Figure 1: Schematic diagram of SLM reactor
(Source: Anupama and Palanivelu 2005)

Instrumentation

CVAFS (Model: 10.025, Millennium Merlin, PS analytical London) was used for the determination of mercury concentration in the feed and strip side of the reactor. The instrument works on the principles of fluorescence with the

measurement range of 0.1-1000 ppb of mercury (Figure 2). Samples were initially subjected to acidification which was followed by reduction with 20% stannous chloride. The vapours thus formed were carried to the detector where they fluoresce.

3. RESULTS AND DISCUSSION

Characterization of the wastewater sample

Initial pH of the wastewater sample was found to be 6.5 \pm 0.2. It was then acidified with 5% HNO₃ for further heavy metal analysis in ICP-OES. The results obtained are presented in Table 1. Aluminium was found to be in high concentration in the sample followed by iron. Lead and nickel were in significant concentration. Cadmium, chromium, copper, antimony and arsenic were less than the detection limit.



Figure 2: Picture of CVAFS

Table 1: heavy metal concentration in the wastewater sample

Parameters	Concentration (ppb)
Lead	220
Nickel	140
Iron	608
Aluminium	448000
Cadmium	BDL
Chromium	BDL
Copper	BDL
Antimony	BDL
Arsenic	BDL

BDL- 0.002 ppm

Removal efficiency

Initial concentration of mercury ions in the wastewater was determined to be 18 ppb. The level of mercury in the wastewater was above the permissible standards (5 ppb). Samples collected at various time intervals were subjected for the determination of concentration of mercury ions using

CVAFS and the results are shown in Figure 3. From the figure, it could be easily noted that the removal process was very fast and the entire mercury ions were removed in about 10 minutes of reaction time.

Removal efficiency of the SLM reactor was determined using the formula shown in equation 1, wherein C_f and C_s represent the concentration of mercury (Hg^{2+}) ions present in the feed phase and strip phase, respectively. Thus in five minutes of reaction time about 63% of removal efficiency was achieved. The remaining ions were completely transported to strip side in ten minutes. Hence, 99% removal of Hg^{2+} ions requires only 10 min by this study.

$$\text{Removal efficiency (\%)} = \frac{C_f - C_s}{C_f} \times 100 \quad (1)$$

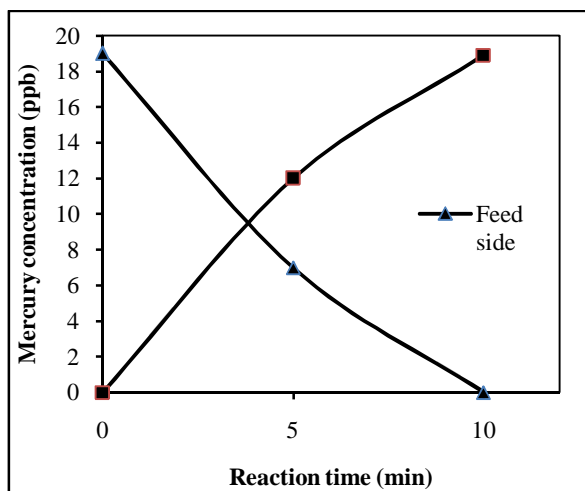


Figure 3: Transport of mercury (Hg^{2+}) ions from feed to strip side.

4. CONCLUSION

About 99% of mercury ions can be removed in ten minutes of reaction time using this study. The use of TBP based SLM reactor has been demonstrated to be an effective method for the removal of mercury ions in traces. This type of treatment method can be incorporated in power plants for the overall management of mercury emission.

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