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UNIVERSITY OF SOUTHAMPTON  
FACULTY OF ENGINEERING, SCIENCE & MATHEMATICS  
School of Civil Engineering and the Environment

**The use of fly ash to stabilise low concentrations of mercury in  
the environment**

by

Waraporn Kitchainukul

Thesis for the degree of Doctor of Philosophy

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UNIVERSITY OF SOUTHAMPTON

**ABSTRACT**

FACULTY OF ENGINEERING, SCIENCE & MATHEMATICS  
SCHOOL OF CIVIL ENGINEERING AND THE ENVIRONMENT

**Doctor of Philosophy**

**THE USE OF FLY ASH TO STABILISE LOW CONCENTRATIONS OF  
MERCURY IN THE ENVIRONMENT**

**By Waraporn Kitchainukul**

The work investigates if fly ash from Ekibatuz Power Plant can stabilise low concentrations of mercury in the environment and prevent it from becoming soluble in water and in preventing it transforming into the methylated form.

The work demonstrates that mercury bound to fly ash from the coal fired 4,000 Mwatt Ekibatuz Power Plant in Kazakhstan is fairly stable at pH levels that are found in most natural water bodies. The adsorption behavior followed the Freundlich adsorption model. The adsorption capacity of the fly ash for Hg (II) was found to be  $3.0 \text{ mg.g}^{-1}$  of dry ash, the adsorption equilibrium being reached after 96 hours. The adsorption kinetic and studied at pHs between 6 and 8. The study showed that between the pH range of 6.0 and 8.0 bound mercury on wet and air dried ash was fairly resistant to leaching with the maximum leaching being  $0.292 \text{ mg.l}^{-1}$  and  $0.14 \text{ mg.l}^{-1}$  for the wet and air dried fly ash, respectively, with leachate at pH 7.0.

Laboratory studies of the stability of the adsorbed mercury on fly ash when mixed with organic rich sediments in an anaerobic environment at pH 7.0 showed that despite ideal conditions for methylation to take place after 8 weeks, the concentration in solution was less than  $2 \text{ }\mu\text{g.l}^{-1}$ . The studies showed that unburnt carbon contained in raw fly ash was the key factor for adsorption reaction. The results indicated that fly ash from the 4,000 Mwatt Ekibatuz Power Plant in Kazakhstan fired with high ash medium volatile coal can be used to stabilise low concentration of mercury in the natural aquatic environment.

Keywords: Mercury, Methylmercury, Fly ash, Stabilisation, Aquatic environment,

Adsorption isotherm

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## DECLARATION OF AUTHORSHIP

I, **Waraporn Kitchainukul**, declare that the thesis entitled '**The use of fly ash to stabilise low levels of mercury in the environment**' and the work presented in the thesis are both my own, and have been generated by me as the result of my own original research. I confirm that:

- this work was done wholly or mainly while in candidature for a research degree at this University;
- where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
- where I have consulted the published work of others, this is always clearly attributed;
- where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;
- I have acknowledged all main sources of help;
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself;
- none of this work has been published before submission,

Signed:.....

Date:.....

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## Units and Abbreviations

Hg	Mercury
Hg <sup>0</sup>	Elemental mercury
Hg <sup>+</sup>	Mercurous
Hg <sup>++</sup>	Mercuric
Hg <sub>p</sub>	Mercury particulate
Hg <sup>1+</sup>	Monovalent mercury
Hg <sup>2+</sup>	Divalent mercury
mg.g <sup>-1</sup>	Milligram per gram
mg.l <sup>-1</sup>	Milligram per litre
µg.l <sup>-1</sup>	Microgram per litre
ng.l <sup>-1</sup>	Nanogram per litre
t y <sup>-1</sup>	Ton per year
E <sub>h</sub>	Redox potential
mV	Millivolt
µmol	Micro molar
nmol	Nano molar
mmol	Milli molar
v/v	Volume by Volume
rpm	Revolutions per min.
d.w.	Dry weight
DI	Deionised

# Chapter 1

## Introduction

### 1.1 Background

Coal burnt in coal fired power plants is the World's major source of mercury pollutants in the environment. During the burning process, the Hg in the coal is released into the atmosphere mainly as  $\text{Hg}^{++}$  vapourises in the flue gases, but small amounts remain in the fly ash. The amount of Hg released is dependent on the source of coal, with American mined coal being particularly rich in mercury (Baird and Cann, 2005). However, the amount of Hg in the flue gas also depends on the coal types and composition, and on combustion and flue gas conditions (Kotnik 1999). Depending on the gas composition, fly ash is able both to adsorb mercury and to oxidize elemental mercury in the flue gas (Nriagu and Pacyan, 1988). Hence the fraction of mercury released into the atmosphere is dependant on combustion conditions. Chu and Porcella (1995) and Hoffart et al. (2005) reported that after coal combustion about 5% of mercury persisted in slag and ash; and 95% of mercury was emitted through the stacks. Zhuang et al. (2000) and Rio and Delebarre (2003) found that elemental mercury could be oxidized and adsorbed on the surface of fly ash particles.

Mercury is an extremely toxic substance and its pollution is widespread in our environment with anthropogenic sources of mercury polluting to some extent the entire earth's air, soil and water resources. Dangerous concentrations of mercury only occur, however, near point sources or where it bio accumulated in the food chain (USEPA1998; Ullrich, et al., 2001). Fahlek and Bursik (1995) stated that elemental mercury is evenly distributed throughout the troposphere because of its long residence time. After oxidation to divalent water-soluble Hg compounds, the residence time decreases to a few days as it is washed out by rain, but the divalent mercury ( $\text{Hg}^{2+}$ ) compounds can be deposited both by wet deposition and in dry form. Mercury in the organic forms can be accumulated in the food chain and is highly toxic at very low concentrations. The central nervous system is the main target for

methylmercury affecting the sensory, visual and auditory functions. Low doses can create non-specific symptoms such as paresthesia (tingling of the extremities), malaise, or blurred vision. Higher doses can cause deafness, loss of coordination when walking, and speech disorders, and in the worst cases, coma and death (Baird and Cann, 2005).

The most problematic sources of mercury pollution occur when it bio accumulates in the aquatic food chain, with unacceptable concentrations of mercury being found in predatory fish or animals, such as seals or Tuna or polar bears, as well as Arctic people (Baird and Cann, 2005). If this bio accumulation is to be controlled, it is essential to break the source-pathway-target link, and the most logical point is to try to break the link between the source and the first link; in other words, the inorganic source of pollution and its bio methylation. The United States Environmental Protection Agency (USEPA), proposed regulations in 2003 requiring coal fired power plants to install air pollution treatment devices which would remove mercury from exhaust gases before being emitted into the air due to the environmental problem in the U.S.A, particularly the high concentration of Hg accumulation in fish. The elemental mercury in the atmosphere can also undergo transformations into inorganic and organic mercury forms. The most common natural forms of mercury found in the environment are metallic mercury, mercury sulfide, mercuric chloride, and methylmercury. Some micro-organisms and natural processes can change the mercury in the environment from one form to another (UNEP, 2003).

Fly ash from coal fired power plant is other important pollutant. Coal fired power plant is a major anthropogenic sources which produced large amount of fly ash. The American Coal Ash Association, ACAA (2002) reported that in the U.S.A alone the electricity utilities used 128.7 million tons of coal which produced approximately 76.6 million tons of fly ash. Fly ash is the material obtained from dust collection devices which remove particulate matter from the flue gases. Coal-fired power plant ash contains both the combustion solids of coal mineral matter from coal, and unburnt carbon. The type of fly ash depends on the type of coal and the manner in which the burnt ash is collected. Approximately one-third of the fly ash produced is utilised in cement, concrete, structural fill, waste stabilisation and road base stabilisation, whereas the rest is disposed of in landfill (Komnitsas et al., 2004; Wang et al., 2004). However, some research has found that fly ash could be used as

adsorbent material to remove some pollutants from wastewater treatment such as Chemical Oxygen Demand (COD), dye, and heavy metals (Wang and Wu, 2006; Cetin and Pehlivan, 2007; Alinnor, 2007; Sahu et al., 2008). Rio and Delebarre (2003) suggested that fly ash has the potential for remediation techniques particularly immobilisation of mobile forms of mercury by adsorption process. The adsorption is the process of accumulating materials that are in solution on an interface, which may be liquid-liquid, liquid-solid, gas-liquid or gas-solid. An adsorption capacity of fly ash for a particular contaminant can be determined by developing its adsorption isotherm. The equilibrium adsorption models, which used are the Langmuir isotherm and the Freundlich isotherm (Weber and With, 1972). The Freundlich isotherm was deemed appropriate for mercury adsorption on fly ash as it represent initial surface adsorption followed by a condensation effect resulting from extremely strong solute-solute interaction. This is the case for mercury as much of the adsorbed mercury remains different to desorbs shown in Chapter 4.

This study will establish the optimum conditions of fly ash to stabilise soluble mercury and how tightly mercury is bound to fly ash by using adsorption reactions. The tightness of mercury bound will test the leaching of mercury from wet and air dried spent fly ash (mercury loaded fly ash). It will go on to establish if the ash can be used to stabilise low concentrations of mercury in the aquatic environment and if it could present a low cost option to break the first link of mercury cycle which contaminated into the food chain.

## **1.2 Aim**

The purpose of this investigation was to determine the effectiveness of fly ash in adsorbing and stabilising low concentrations of mercury in the natural aquatic environment by lowering the concentration in the water column to a level that would no longer pose an environmental threat. The initial part of the study looks at its stability to physical condition: pH 6 to 8, fly ash dosage, contact time and initial mercury concentration. The second part of the study looks at ability of fly ash to stabilise mercury in sediment with potentially methylating sediments with anaerobic organic rich methylated conditions at pH 7.0. The effect of unburnt carbon on the adsorption process was investigated.



### **1.2.1 Objectives of adsorption process study**

To determine the adsorption and desorption kinetics of Hg on fly ash from the 4,000 Mwatt Ekibatuz, a power plant in Kazakhstan fired with high ash, medium volatile coal to establish if fly ash can be used to stabilise mercury in the natural aquatic environment. This was achieved by the following:

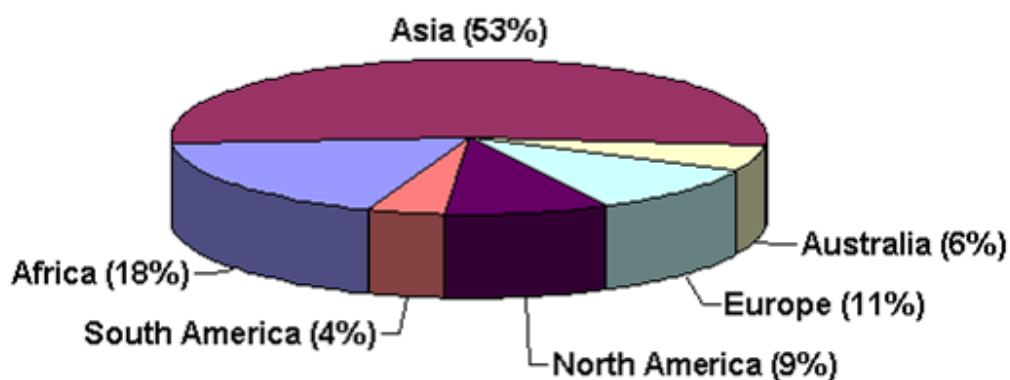
- a) Carrying out adsorption experiments which both established the adsorption capacity and the Freundlich adsorption/desorption isotherm for both wet and air dried fly ash.
- b) pH is known to affect the stability of adsorbed mercury. The effect of pH between 6 and 8 on the ability of fly ash to adsorb mercury was investigated. pH 6 to 8 represents the common range of many naturally occurring water bodies.
- c) Investigation to determine if fly ash can reduce the solubility of mercury under anaerobic condition in the presence of organic rich sediment at pH 7.0
- d) Unburnt carbon in the fly ash is expected to play an important role in the adsorption process. An experiment was conducted to establish the importance of unburnt carbon in the ash on the adsorption process.

## Chapter 2

### Literature review

#### 2.1 Sources of Mercury in the environment

Mercury in the atmosphere has come from both natural and anthropogenic sources. The mercury emissions from natural sources are due to mercury minerals in the Earth's crust, during volcanic activity, through weathering of rocks (Wangberg et al., 2007), and especially cinnabar, while the anthropogenic mercury emissions are due to human activities such as coal power plants, chlor-alkali, cement and metal production, and fluorescent lighting. Table 2-1 and Figure 2-1 summarises the estimation that has been made of mercury emission in different parts of the world and geographic regions. The United States Environmental Protection Agency, USEPA (1998) reported that approximately a third of the current worldwide mercury emissions to air are from natural sources, with anthropogenic emissions accounting for the remaining two-thirds. Pirrone et al., (2001) estimated the Hg fraction of the chemical inorganic species of mercury ( $\text{Hg}^0$ ,  $\text{Hg}^{2+}$ , and  $\text{Hg}_p$ ) from different anthropogenic sources, Table 2-2. Although these estimates are highly uncertain, they indicate that the most important mercury emission source is coal combustion.



**Figure 2-1 Mercury emission in different parts of the world**

Source: Presentation by Pacyna and Munthe at mercury workshop in Brussels,  
March 29-30, (2004)

**Table 2-1 Summary of estimates of mercury emissions ( $t\ y^{-1}$ ) estimation**

Information source	Region/ Country	Natural Source, ton/annum	Anthropogenic Source, ton/annum		
			Coal Combustion	Coal fire Power plant	Other
EPA, (1998)	U.S.A	-	263	51	-
CNEPA, (2000)	China	-	213.8	-	-
Pacyna, (2002)	China	-	500		
Pirrone et al., (1996) and Lamborg et al., (2002)	global	1,500-2,000	2,000-3,500		
Seigneur et al., (2004)	global	-	2,000-2,200		
Jaffe et al., (2005)	Asia	-	More than 1,000-1,100		

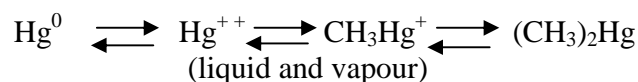
**Table 2-2 Emission profiles (fraction of the total) of different forms of Mercury from a number of different anthropogenic sources (table from Pirrone et al., 2001)**

Species	Coal Combustion Power Plants	Coal Combustion Residual Heat	Oil Combustion	Cement Production	Non-Ferrous Metals	Pig & Iron	Chlor alkali	Waste Incineration	Other	Ave. of all sources	Information Source
Hg <sup>0</sup> (gas)	0.5	0.5	0.5	0.8	0.6	0.8	0.7	0.2	0.8	0.64	Pacyna et al., (2000)
Hg(II)	0.4	0.4	0.4	0.15	0.3	0.15	0.3	0.6	0.15	0.285	Modified by Pacyna (1998)
Hg <sub>p</sub>	0.1	0.1	0.1	0.05	0.1	0.05	0	0.2	0.05	0.075	-

## 2.2 Mercury in the environment

Mercury is a heavy liquid silver metal at ordinary temperatures. It is rarely found as pure liquid metal mercury in nature but rather within compounds and inorganic salts. It can be bound to other compounds as monovalent or divalent mercury (Hg<sup>2+</sup>). A number of inorganic and organic compounds of mercury can be formed from divalent mercury (United Nations Environment Programme (UNEP), 2003). Mercury in the environment mainly originates from flume gas coal fired power plants but also from a lesser extent, from old chlor-alkali plants, fluorescent lights and mercury batteries. The forms of Hg emission from burning coal at temperatures above 150°C are mainly metallic mercury, mercuric sulfide (HgS), and organometallic compounds (Finkelman, 1981; Swaine, 1990). The mercury forms released from power plants can be in different oxidation states such as Hg<sup>0</sup> or Hg<sup>2+</sup> but most is mercuric oxide (HgO). Their ratios depend on coal type and composition, and on combustion and flue gas conditions. Elemental Hg (Hg<sup>0</sup>) and divalent Hg (Hg<sup>2+</sup>) are the major forms that exist in the atmosphere. Hg<sup>0</sup> has a longer atmosphere lifetime (0.5-2 years) than Hg<sup>2+</sup> (hours or a few days). It is, therefore, not surprising that it can be transported long distances in the atmosphere and contributes to Hg cycling at a global scale (USEPA, 1997b; Senior, 2001).

Hartung and Dinman (1972) reported that the three main forms of mercury released into the aquatic system are elementary mercury ( $\text{Hg}^0$ ), bivalent inorganic mercury ( $\text{Hg}^{++}$ ), and phenylmercury, all these compounds tend to rapidly move into the sediments. Elementary ( $\text{Hg}^0$ ) is insoluble whereas bivalent mercury forms strong complexes with many organic and inorganic substances. When elemental mercury is oxidized to phenylmercury and broken down, under anaerobic conditions the mercuric ion can be methylated to monomethylmercury or dimethylmercury. The different forms of mercury metal, inorganic salts and organic forms of mercury all exist in the environment, the relative abundance of each depending on environmental conditions, with the equilibrium changing between air, aquatic aerobic and anaerobic conditions, and in soils.

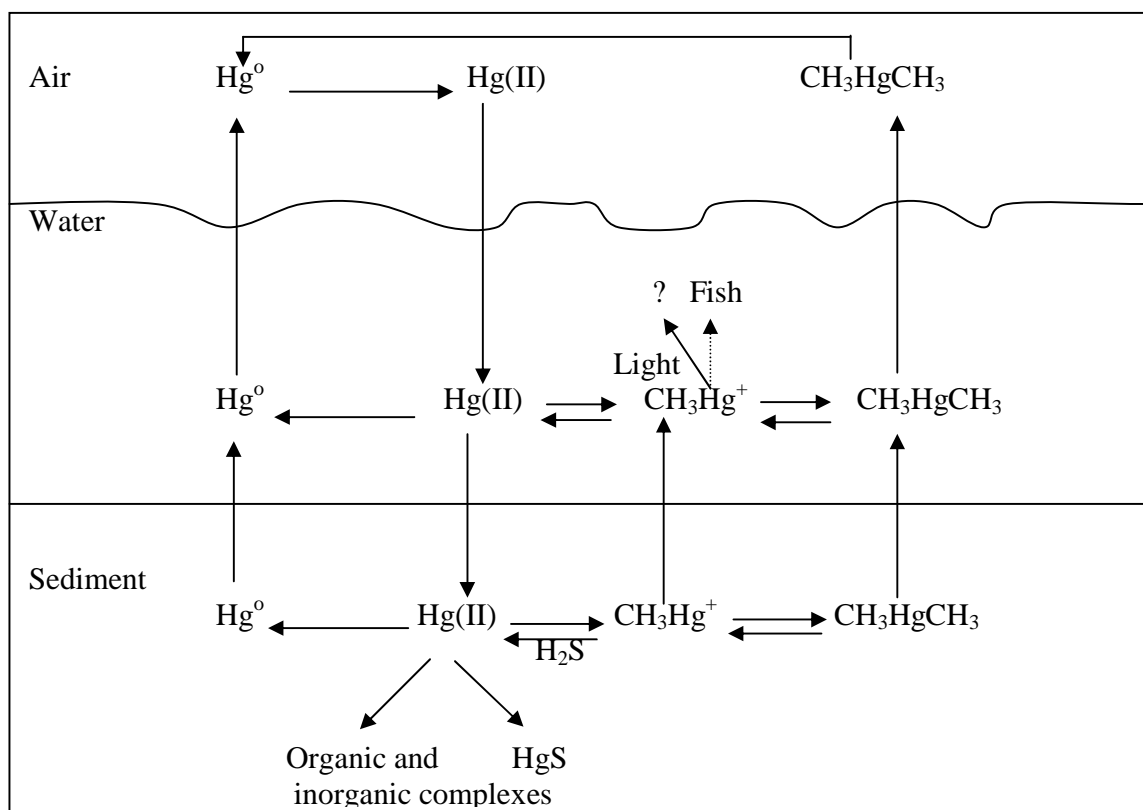


Ullrich et al., 2001 reported that approximate 10% to 30% of the dissolved mercury in the ocean is present as elemental mercury and similar concentration have been found in freshwater. The main dissolved Hg species are elemental mercury, complexes of mercury with various inorganic and organic ligands, and organic mercury forms, mainly methylmercury and dimethylmercury (Ullrich et al., 2001). When mercury is deposited on land or water, it can be transformed into methylmercury in anaerobic condition, and other organic forms that can then enters the food chain. Methylmercury are highly toxic because its compounds are covalent molecules, they are soluble in animal tissue and can pass through biological membranes. Humans are mostly exposed to methylmercury by consuming fish. Minamata disease, for example, is the incident of mercury poison. The notorious incidents of mercury poisoning occurred in the 1950s at Minamata Bay and in the 1960s on the Agano River in Japan (Ullrich et al., 2001). In 1956, 1960 and 1972, hundreds of deaths in Iraq and a few in China and the United States, resulted from the consumption of bread made from seed gain that had been treated with mercury-based fungicides to seduce seeding losses from fungus attack (Baird and Cann, 2005).

### 2.3 Mercury methylation

The real danger to living organisms comes from the presence of alkylmercury compounds, generally methylmercury, in the environment. Fish, high plants and animals cannot, themselves, convert other mercury compounds into methylmercury, but microorganisms (bacteria) in bottom sediment and aerobic soil can do so. The methylmercury can then be taken up by aquatic organisms and concentrated in the food chains. This results in high concentrations of mercury in fish in contaminated waters, mainly in the form of methylmercury. Methylmercury compounds are mostly absorbed by the gastrointestinal tract. They will be stored in the body fat (lipids) and have considerable stability in the animal body. The biological half-life of these compounds in human beings is about 70 days. The concentration of Hg of 8 ppm or over in the brain can cause poisoning (Saha and Mckinlay, 1975). Baird and Cann (2005) stated that the process of dimethylmercury formation occurred in the muddy sediments of rivers and lakes, especially under anaerobic conditions. The methylation of inorganic mercury by bacteria is influenced by many factors in the aquatic environment such as; redox potential ( $E_h$ ), pH, inorganic complexing agents' concentration, microbial activity, chlorides and sulfate, and the bioavailability of Hg (Baird and Cann, 2005). The less volatile mixed compounds  $\text{CH}_3\text{HgCl}$  and  $\text{CH}_3\text{HgOH}$ , collectively called methylmercury (or monomethylmercury), are often written as  $\text{CH}_3\text{HgX}$ , or somewhat misleadingly as  $\text{CH}_3\text{Hg}^+$ . These substances, like most of those written as  $\text{Hg}^{2+}$ , consist of covalent molecules, not ionic lattices. (The methylmercury ion  $\text{CH}_3\text{Hg}^+$  exists as such only in compounds with anions such as nitrate or sulfate) (Baird and Cann, 2005).

Monomethylmercury production predominates over dimethylmercury formation in acidic or neutral aqueous solutions. Dimethylmercury evaporates from water relatively quickly unless it is transformed by acidic conditions into the monomethyl form (Baird and Cann 2005). The pathways for the production and fate of dimethylmercury and of other mercury species in a body of water are illustrated in Figure 2-2.



**Figure 2-2: The pathways for the production and fate of dimethylmercury and of other mercury species in a body of water [Source: Adapted from Winfrey and Rudd, 'Environmental Factors Affecting the Formation of Methylmercury in Low pH Lakes,' *Environmental Toxicology and Chemistry* 9 (1990): 853-869]**

Methylmercury in surface water is photodegraded (to as yet unknown products). Wiener et al. (2003) pointed out that the photo degradation of mercury end products had not been determined. Theoretically, three oxidation stages of mercury could occur, but  $\text{Hg(II)}$  could be methylated again, while  $\text{Hg}^0$  could evaporate from the lake to the atmosphere. Ullrich (2007) reported that the mercury content of fish in lakes is generally greater in acidic water, probably because both the solubility of mercury is greater and the methylation of mercury is faster at lower pH. In this way, the acidification of natural waters indirectly increased the exposure of fish-eaters to methylmercury. The half-life of methylmercury compounds in humans is about 70 days which is much longer than that for  $\text{Hg}^{2+}$  salts, due in part to its greater solubility in a lipid environment. Consequently methylmercury can accumulate in

the body to a much higher steady-state concentration, even if, on a daily basis, a person consumes an amount that individually would not be harmful (Barid and Cann, 2005).

#### **2.4 Factors affecting methylation and demethylation in the aquatic environment**

The synthesis of methylmercury (MeHg) in aquatic systems is influenced by a broad variety of environmental factors such as; temperature, redox potential ( $E_h$ ), pH, inorganic and organic complexing agents' concentration, microbial activity, chlorides and sulfate (Winfrey and Rudd, 1990; Gilmour and Henry, 1991; Craig, 1986; Barkay et al., 1997). The net methylmercury concentrations in the environment are a result of the opposite processes of methylation and demethylation.

Ullrich et al. 2001 reported that microorganisms play an important role in aquatic mercury cycling and catalyse many of the interconversions between different forms of mercury, such as converted  $Hg^{2+}$  to methyl and dimethyl mercury and reduced  $Hg^{2+}$  to  $Hg^0$ . Mercury compounds, in fact, are toxic to freshwater microorganisms. However, many bacteria have developed to resistance mechanism. A large number of organisms, including strict, facultative anaerobes and aerobes have been shown to methylate Hg in vitro (Ullrich, 2007).

Temperature affects methylation as a result of its effect on the overall microbial activity. Moderately high temperature has a stimulating effect on mercury methylation by increasing microbial activity (Ullrich et al., 2001). Several studies have shown greater methylation activities during mid or late summer months (Callister and Winfrey, 1996; Korthals and Winfrey, 1987). Ullrich (2007) reported that mercury methylation activity in sediment is often correlated with the distribution of sulfate reducing bacteria, SRB population. Fukui and Takii (1989) reported that increased temperature stimulated the growth of SRB, then therefore possibly affected the production of methylmercury. Callister and Winfrey (1996) observed that 35°C was optimum temperature for mercury methylation. However, temperature is not the only factor that controls mercury methylation.

In 1984, Compeau and Bartha found that mercury methylation in estuarine sediment were favored at -200 mV than at +110 mV. A higher rate of methylation in the anaerobically



incubated sediment than the aerobically incubated sediment was found by Callister and Winfrey (1986). Gagnon et al. (1996) observed that the higher methyl mercury concentration in pore water extracted from anoxic sediment than that from oxic sediment. This is almost certainly the result of anaerobic conditions favour methylation. On the other hand, mercury demethylation or degradation of methyl mercury occurs more rapidly under aerobic conditions (Compeau and Bartha, 1984; Olson and Cooper, 1976). Baird and Cann (2005) found that the process of dimethylmercury formation occurred in the muddy sediments of rivers and lakes, especially under anaerobic conditions. Årne, (1972) reported that the methylation activity very often was higher under anaerobic conditions than under aerobic condition, and microbe were the important factor for methylation. Fagerstrom and Jernelov (1972) found that freshwater sediment had higher  $\text{Hg}^{2+}$  methylation activity and higher persistence of methylmercury under anaerobic condition than aerobic incubation condition. Both methylation rates and the stability of methyl mercury in sediments appear to be enhanced under anaerobic conditions, in contrast to methylation rates under aerobic conditions. These may because of the reduced activities of anaerobic sulfate reducing bacteria.

The effect of pH on mercury methylation in sediment is uncertain. Some studies indicated that decreased pH could inhibit the mercury methylation but others indicated that decreased pH could enhance the formation of mercury methylation. For example, Kelly and Rudd (2003) showed that bioaccumulation was positively correlated with the concentration of  $\text{H}^+$  (decreasing pH). The uptake of both charged and uncharged mercury species was increased with high concentration of  $\text{H}^+$  (decreasing pH). In contrast, Ramlal and Rudd (1985) and Steffan and Korthals (1988) found that mercury methylation production in sediment decreased when decreasing pH from 7 to 4.5. Steffan and Korthals (1988) found that mercury methylation was inhibited more than 65% when the sediment was acidified to pH 4.5.

In 2006, Lambertsson and Nilsson found that the concentration of methylmercury was affected by organic matter which influenced microbial activity and controlled the partition of Hg between solid and dissolved phase by serving as complexing agents for  $\text{Hg}^{2+}$  and methylmercury. They indicated that concentration of total mercury ( $\text{Hg}_{\text{tot}}$ ) and redox

potential influence the relative importance of reductive and oxidative demethylation pathways. Reductive demethylation seems to predominate in mercury contaminated water under aerobic condition, while oxidative demethylation mainly occurs in unpolluted anoxic sediment. Oxidative demethylation end product is  $\text{Hg}^{2+}$ . On the other hand, reductive demethylation is no net elimination of  $\text{Hg}^{2+}$  takes place in this process. Anoxic sediment may therefore be subjected to higher degrees of methyl mercury accumulation compared to Hg contaminated sediment as a result of substrate ( $\text{Hg}^{2+}$ ) recycling. King and Kostka (2000) and Lambertsson and Nilsson (2006) reported that organic rich sediment with low redox potential increased production and mercury methylation rate, and then increased the accumulation of methylmercury in sediment. Several researches reported that organic matter in fresh and marine sediments had a positive effect on mercury methylation (Callister and Winfrey, 1986; Choi and Ctiase 1994; Lambertsson and Nilsson, 2006). High organic contents in the sediment are a prerequisite for maintaining low redox potentials, supplies electron donors for SRB and concomitant mercury methylation.

The controlling factors of Hg accumulation in aquatic biota are not well understood. Normally, accumulation of methylmercury is explained by its high stability and lipid solubility, and high binding to  $-\text{SH}$  groups associated with protein (Ullrich et al., 2001). However, several studies have pointed out that the sulfide concentration could be a limiting factor for mercury methylation and that potential mercury methylation rates are positively correlated with reduction rates (Wu, 2006). Mercuric sulfide ( $\text{HgS}$ ) is main insoluble ( $L_{\text{HgS}} = 10^{-53} \text{ mol}^2 \text{ l}^{-2}$ ) inorganic Hg compound in aquatic systems. Mercuric oxide ( $\text{HgO}$ ), which is sparingly soluble ( $10^{-4} \text{ mol l}^{-1}$ ) is also commonly encountered in contaminated environment.  $\text{HgS}$  formation is generally favored at low pH and low sulfide concentration. Under low  $E_h$  and high pH conditions, or an excess of sulfide ions is present  $\text{HgS}$  can be converted to soluble Hg-S complexes such as  $\text{HgS}^{2-}$ . Organic matter also enhances the solubility of  $\text{HgS}$  and may lead to a significant release of Hg into solution. Previous studies suggested that mercury in  $\text{HgS}$  form is not available for bacterial methylation under anaerobic condition (Ullrich et al., 2001). This confirmed by the finding of Compeau and Bartha (1984), Gilmour and Riedel (1998) and Berman and Bartha (1986). They reported that inhibited mercury methylation by controlling the bioavailability of mercury. High sulfide often builds up in the anaerobic sediment with organic rich matter and sea salt.

Gilmour and Riedel (1998) found that greater than 10  $\mu\text{M}$  of dissolved sulfide inhibited methylation due to the precipitation of mercury. Berman and Bartha (1986) observed that 1.98  $\text{mg g}^{-1}$  of free sulfide reduced methylation in the freshwater sediment and the methylation was recovered when the sulfide in the sediment was diluted.

Gotgeberg and Greger (2006) studied formation of methylmercury in the aquatic macrophyte water spinach (*Ipomoea aquatica*) and found that most of the Hg taken up by plants was bound in the roots. Sunderland et al. (2006) reported that methylmercury production by sulfate reducing bacteria in coastal sediments lead to mercury bioaccumulation in fish, shellfish, and ultimately humans. Sulfur, organic carbon, and sediment structure and composition are affected by methylmercury production by changing the amount of bioavailable inorganic mercury and by stimulating the activity of methylating microbes. However, other types of bacteria can also methylate mercury as effectively as sulfate reducing bacteria (SRB). In 2006, Fleming et al., found that an iron-reducing bacterium, *Geobacter* sp strain CLFeRB, produced a significant amount of methylmercury in the freshwater sediment in Clear Lake, CA.

## **2.5 Effects of Mercury on health**

Mercury is the most volatile of metals, and its vapour is highly toxic. Mercury vapour consists of free, neutral atoms. It diffused from the lungs into the bloodstream, and then, because of its electrically neutral, it readily crosses the blood-brain barrier to enter the brain, where it is transformed to the  $\text{Hg}^{2+}$ . Liquid mercury itself is not highly toxic, and most of that ingested is excreted (Baird and Cann, 2005). Methylmercury is, in fact, the most hazardous form of mercury, followed by the vapour of the element. Fusako and McCormack, (2004) reported that the central nervous system, which is manifested by difficulties with coordination, eyesight, and tactile senses, was the main target for methylmercury. In the brain methylmercury is converted to inorganic mercury, which is probably responsible for brain damage.

The most common form of the mercury presented in humans is methylmercury. Almost all of it originates from the fish consumption, particularly oily fish. 80% of the mercury is methylmercury, of which about 95% is absorbed by the body when the fish is eaten.

Methyl mercury can bind to the sulfhydryl group in proteins and is therefore distributed throughout the fish. Thus, the mercury-containing part cannot be eliminated before the fish is eaten. Fish absorb methyl mercury that is dissolved in water as it passes across their gills and their food supply (the United Nations Environment Programme (UNEP), 2003; Hightower and Moore, 2003; Baird and Cann, 2005).

In 1953, Minamata disease was first recognized as methylmercury poisoning via bioaccumulation in aquatic food chains at Minamata, Japan. 111 people were poisoned after eating sea food containing high concentration of methylmercury (27-102 ppm dry weight). The second Minamata disease epidemic broke out in the Agano River region in Niigata prefecture in Japan in 1964-65. 26 people were poisoned after eating sea food contaminated with methylmercury compounds and 5 died (Frei and Hutzinger, 1975). By 1956, it was shown that the populations were suffering from Hg poisoning due to the ingestion of fish and shellfish from the Minamata bay (Gochfeld, 2003). In 1959, the Hg contamination was extraordinarily high up to  $2,010 \text{ mg.l}^{-1}$  in mud near the drainage channel of Chisso (Minamata Bay), and the Hg content only moderately declined with increased distance from the channel. Fish and shellfish in the bay contained high Hg concentrations. The cause was Hg effluent from the Chisso chemical plant's acetaldehyde production where inorganic  $\text{HgSO}_4$  was used as a catalyst and methylated in the sediments of the bay (Harada, 1995). Clarkson et al., (2003a) estimated that the amount of discharged Hg was 456 tons of Hg of which about one ton of MeHg was formed between 1932 and 1968.

Another Hg poisoning episode happened in Iraq during 1971 to 1972 in the winter. Wheat seeds for crop planting, which had been treated with MeHg as a fungicide, were distributed in the rural areas. The seeds were ground for making flour and baked into bread. The bread was contaminated with MeHg, and consequently damaged the local people's health. The susceptibility of the fetus to in-utero exposure to methyl mercury was also observed in this outbreak. Thirty-three infants had abnormal neurological scores and eight infants were born to mothers whose hair had Hg concentration between 10 and  $20 \text{ mg l}^{-1}$ .

Clearly since the organic form of mercury is the most toxic and is the cause of most of the mercury encountered in man, it is important to control its up take by breaking the

source/path/receptor path way. The main source of up take in human is fish, therefore it is important to stop fish accumulating it from the water. A significant point to break the pathway is to stop mercury being solubilised as methyl mercury from the substrate.

## **2.6 Mercury treatment technologies in aquatic and soil environment**

There are a number of possible technical approaches to remove mercury, but there is not one single best technology that can be applied broadly to any Hg pollution incident (Pavlish and Mann, 1998). Combination of available control methods could provide over 90% removal efficiency for some plants, but not for others. In 1997, The USEPA reported technologies and methods for treating aqueous mercury. The technologies used were precipitation (coagulation/co-precipitation with sulfide or coagulant), adsorption process (activated carbon), ion exchange, chemical reduction, and membrane separation. Table 2-3 compares advantages and disadvantages of the mercury treatment technologies (USEPA, 1997, Capsule Report: Mercury Aqueous Treatment).

**Table 2-3 The Mercury treatment technologies comparison**

<b>Mercury Treatment Technologies</b>	<b>Advantages</b>	<b>Disadvantages</b>
<p><b>Precipitation</b></p> <p>- precipitation</p> <p>-Coagulation/ co-precipitation</p>	<p>- Remove inorganic Hg, high percent Hg removal efficiency &gt;99.9%, Range of Hg concentration 10-100 <math>\mu\text{g l}^{-1}</math></p> <p>- Effluent Mercury concentration 10-100 <math>\mu\text{g l}^{-1}</math></p> <p>- Remove both inorganic and organic Hg, 94-98% Hg removal, Range of Hg concentration 50-60 <math>\mu\text{g l}^{-1}</math></p> <p>- Effluent Mercury concentration 0.5-5.0 <math>\mu\text{g l}^{-1}</math></p>	<p>- Large amount of sludge produced by chemical precipitation and co-precipitation reaction.</p> <p>-requiring further management</p>
<p><b>Adsorption process</b></p> <p>Activated Carbon</p>		<p>- Large amount of spent activated carbon and concurrently recovery of mercury is not addressed in the literature although it can be vaporized and condensed</p> <p>- Expensive and requiring further management</p>

**Table 2-3 The Mercury treatment technologies comparison (Continued)**

<b>Mercury Treatment Technologies</b>	<b>Advantages</b>	<b>Disadvantages</b>
- Granular activated Carbon (GAC)	<ul style="list-style-type: none"> <li>- More than 41% Hg removal, Range of Hg concentration 0-100 <math>\mu\text{g.l}^{-1}</math>, May regenerated or the spent carbon can be replaced</li> <li>- Effluent Mercury concentration 0.5-20 <math>\mu\text{g.l}^{-1}</math></li> </ul>	
- Powder activated Carbon (PAC)	<ul style="list-style-type: none"> <li>- 60 % Hg removal, Range of Hg concentration 1.0-10,000 <math>\mu\text{g.l}^{-1}</math>,</li> <li>- Effluent Mercury concentration 0.5-20 <math>\mu\text{g.l}^{-1}</math></li> </ul>	- Not regenerated for reuse
-Coal fly ash	<ul style="list-style-type: none"> <li>- Low cost adsorbent and environmental friendly material</li> <li>- Reduce waste from coal fired power plant</li> <li>- Promising adsorbent for removal of various pollutants</li> <li>- Can be used for gas and water cleaning</li> </ul>	- Large amount of spent fly ash and cannot be replaced.
<b>Ion exchange</b>	<ul style="list-style-type: none"> <li>-Remove mercury in any of its three oxidation states</li> <li>-Operates on demand</li> <li>- Is relatively insensitive to variability</li> <li>- Can achieve essentially a zero of effluent contaminant</li> </ul>	<ul style="list-style-type: none"> <li>-Has potential for chromatographic effluent peaking</li> <li>- Results in spent regenerant brine that must be disposed of</li> <li>- Can yield variable effluent quality</li> </ul>

**Table 2-3 The Mercury treatment technologies comparison (Continued)**

<b>Mercury Treatment Technologies</b>	<b>Advantages</b>	<b>Disadvantages</b>
	<ul style="list-style-type: none"> <li>- Can normally achieve beneficial selectivity reversal upon regeneration</li> <li>- Effluent Mercury concentration 0.5-5.0 <math>\mu\text{g.l}^{-1}</math></li> </ul>	
<b>Chemical reduction</b>	<ul style="list-style-type: none"> <li>- Can be recovered in the metallic state</li> <li>- Effluent Mercury concentration 10- &gt;100 <math>\mu\text{g.l}^{-1}</math></li> </ul>	<ul style="list-style-type: none"> <li>- Cannot effectively achieve mercury concentration below 100 <math>\mu\text{g.l}^{-1}</math></li> <li>-High residual mercury concentration (22-33 <math>\text{mg.l}^{-1}</math>)</li> </ul>
<b>Membrane separation</b>  <ul style="list-style-type: none"> <li>-Ultrafiltration</li> <li>- Charged filtration</li> <li>- Cross flow microfiltration</li> <li>- Magnetic filtration</li> </ul>	<ul style="list-style-type: none"> <li>-Used to remove colloidal material and large molecules with molecular weights</li> <li>- The negative polarization minimizes membrane fouling</li> <li>- Can be reused</li> <li>- 95% removal efficiency</li> <li>- Can be rapidly and efficiently removed</li> <li>- Can be used for removal inorganic Hg at low concentration (5-9 <math>\text{mg.l}^{-1}</math>), and 82-83% removal</li> </ul>	<ul style="list-style-type: none"> <li>- Concentrated brine solution generated from membrane separation process</li> </ul>

Source: USEPA, (1997) Capsule Report: Mercury Aqueous Treatment



Zielonka et al., (2000) reported that the mercury soil contamination problem is very complex as the feature and this contaminant and its behavior in the environment changes from site to site. Mercury concentrations in soil can be as high as several grams of Hg per kg of soil. A number of mercury contamination treatment technologies such as excavation and disposal by using secured landfill, acid leaching, soil washing, stabilisation, amalgamation and thermal desorption are, now, available. However, their applicability varies depending on the form and concentration of mercury in soil. The major disadvantages are very high capital costs and effective only at rather high mercury concentrations. Besides, most reports are for wastewater and sewage sludge rather than soil remediation (Anderson, 1993).

### **2.7 Fly ash as a pollutant adsorbent**

Fly ash is a by-product of coal-fired power plants. The types and amounts of ashes which power plants produce depend on the type of coal and the manner in which the coal is burnt and how the ash is collected. Fly ash is the material obtained from the dust collection devices which remove particulate matter from the exhaust gases.

In general, the particle size of fly ash is within a range of 0.005 mm to 0.074mm. There are three classifications of fly ash classified by American Society for Testing and Materials in the field of pozzolanic material application. The first type is a natural fly ash, while the other two types are anthropogenic fly ash. Three classes of fly ashes are Class-N, Class-C and Class-F. Class N is a natural pozzolan, which is produced by nature, such as volcanic tuff and pumicite. Class-F is fly ash normally produced by burning anthracite or bituminous coal, and Class-C is normally produced from the burning of subbituminous coal and lignite (Hunt 1996, Halstead, 1986). There are also wide differences in characteristics within each class. Coal fired ash contained silicon dioxide ( $\text{SiO}_2$ ), aluminum oxide ( $\text{Al}_2\text{O}_3$ ), alkalies and unburnt carbon therefore, ash able to act as both the adsorption of mercury and the oxidation of elemental mercury in flue gas.

The typical chemistry of coal fired fly ash shown in Table 2-4.

Table 2-4 Typical chemical composition of coal fly ash (in wt %)

	Class-F		Class-C	
	Low-Fe	High-Fe	High-Ca	Low-Ca
SiO <sub>2</sub>	46-57	42-54	25-42	46-59
Al <sub>2</sub> O <sub>3</sub>	18-29	16.5-24	15-21	14-22
Fe <sub>2</sub> O <sub>3</sub>	6-16	16-24	5-10	5-13
CaO	1.8-5.5	1.3-3.8	17-32	8-16
MgO	0.7-2.1	0.3-1.2	4-12.5	3.2-4.9
K <sub>2</sub> O	1.9-2.8	2.1-2.7	0.3-1.6	0.6-1.1
Na <sub>2</sub> O	0.2-1.1	0.2-0.9	0.8-6.0	1.3-4.2
SO <sub>3</sub>	0.4-2.9	0.5-1.8	0.4-5.0	0.4-2.5
LOI	0.6-4.8	1.2-5.0	0.1-1.0	0.1-2.3
TiO <sub>2</sub>	1-2	1-1.5	<1	<1

**Note: LOI (loss on ignition) is presumed amount of carbon content**

**Source: The Fly Ash Resource Center (Majko, 2008)**

The ash with unburnt carbon has potential to adsorb heavy metals and there are reports that a number of the chemical constituents may also adsorb them.

A number of workers have found that fly ash has the ability to adsorb heavy metal since 1975 (Gangoli et al., 1975; Apak, 1998; Shawabkeh et al., 2004; Cetin and Pehlivan, 2007).

Kumar and Dara (1981), and Burba and Willmer (1983) found that fly ash could be a useful adsorbent due to its chemical properties such as SiO<sub>2</sub>, CaO<sub>2</sub>, unburnt carbon, and charcoal. A number of works had looked at the possibility of utilising the properties of fly ash from

coal-fired power plants as cheap adsorbent (Kilgroe et al., 2001, Senior et al., 2004, USEPA, 1999).

Wang and Wu (2006) studied the ability of fly ash to remove inorganic anions from wastewater such as phosphate, fluoride and boron. This study reported that fly ash can be used in wastewater treatment as adsorbent material. It can remove dye, organic compounds, and toxic metal ions from wastewater. Gangoli et al., (1975) for example, investigated the use of fly ash for removing heavy metals from industrial wastewater. They concluded that the adsorption of metal ions adsorbed on fly ash was possible because of its high content of silica and alumina. They also reported that precipitation and/or adsorption processes of fly ash could remove heavy metals from wastewater. Calcium hydroxide in fly ash is alkaline and a precipitation agent for heavy metals and quantities of unburnt carbon, silica and alumina, which are available in fly ash, act as an anion adsorbent in adsorption process.

A number of researches have studied the removal of chromium ions ( $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$ ) using fly ash. Grover and Narayanaswamy, (1982) for example, found that the most effective removal of  $\text{Cr}^{6+}$  occurred at lower pHs. Dasmahapatra et al., (1996) also studied the adsorption of  $\text{Cr}^{6+}$  on fly ash. They found that the removal percentage of  $\text{Cr}^{6+}$  by fly ash was affected by the concentration of  $\text{Cr}^{6+}$  solution, temperature, particle size of fly ash, and pH. The results showed that under acidic condition, increasing chromium ion concentrations and temperatures increased the percent removal of  $\text{Cr}^{6+}$ . However, particle size did not have a significant effect on  $\text{Cr}^{6+}$  removal. Panday et al., (1984) found that the removal efficiency of  $\text{Cr}^{6+}$  from aqueous solution by using a mixture of fly ash and wollastonite (1:1) depended on concentration, pH, and temperature of the solution. The amount of  $\text{Cr}^{6+}$  adsorption was increased with increasing  $\text{Cr}^{6+}$  concentration in solution. The maximum removal of  $\text{Cr}^{6+}$  was  $2.92 \text{ mg g}^{-1}$  at pH 2 and  $30^\circ\text{C}$ . In 2002, Kelleher et al., investigated the removal of  $\text{Cr}^{3+}$  by using fly ash from combustion of poultry litter. They found that the capacity of  $\text{Cr}^{3+}$  adsorption was  $53 \text{ mg g}^{-1}$  at  $20^\circ\text{C}$ . Fly ash adsorption has also been used to treat a number of other metals including Na, K, Mg, Cu, Cd, Mn, Pb, Fe, Ni, and Zn. Panday et al., (1985) studied the removal of copper ion ( $\text{Cu}^{2+}$ ) and found that the removal efficiency was dependent on concentration, pH, and temperature. The

adsorption kinetics indicated the process to be diffusion controlled. The maximum capacity was  $1.39 \text{ mg.g}^{-1}$  at  $30^\circ\text{C}$  and pH 8. Papachristou et al., (1985) used two different fly ashes to determine the selective adsorption of various metal ions (Na, K, Mg, Ca, Cu, Cd, Mn, Hg, Cr, Pb, and Fe). The results indicated that one fly ash sample showed selectivity in adsorbing heavy metal ions from aquatic systems. The selectivity of lead ( $\text{Pb}^{2+}$ ), for example, was 19 meq of  $\text{Pb}^{2+}$  per 100 g of fly ash.

## **2.8 Mercury stabilisation by fly ash**

Since 1985, a number of researchers have found that fly ash from coal combustion residue has potential in environment applications. There was an evidence that fly ash could potentially be used as a low cost adsorbent for removal of mercury ions from the environment (Sen and De, 1987; Kapoor and Viraraghavan, 1992; Banerjee et al., 2005). In 1987, Sen and De, found that the adsorption of Hg on fly ash could be described by using the Freundlich equation. The maximum adsorption of Hg was observed after shaking for 3 hours and optimum pH range was 3.5 to 4.5. They concluded that fly ash from coal combustion was a significant adsorbent when compared with activated powdered charcoal. Kapoor and Viraraghavan (1992) studied the adsorption of mercury from wastewater by bentonite. They concluded that the optimum condition was 4 hours for contact time at pHs between 3.0 to 3.5 and the adsorption behaviour followed the Freundlich model. Banerjee et al. (2005) studied the removal of Cr (VI) and Hg (II) from aqueous solutions using fly ash and impregnated fly ash. They found that fly ash had a potential to remove both Cr (VI) and Hg (II) as low-cost adsorbent. The study used the batch equilibration technique. The adsorption efficiency was depended on initial concentration and adsorption behaviour following the Langmuir adsorption model. The maximum adsorption capacity of fly ash was  $1.379 \text{ mg.g}^{-1}$  for Cr (VI) and was  $11.00 \text{ mg.g}^{-1}$  for Hg (II).

Karatza et al. (1998) indicated that using a fabric filter to collect fly ash from municipal solid waste (MSW) incinerators may promote Hg emission control. Carey et al., (2000) studied the adsorption isotherm in a fixed bed reactor at temperatures between  $150$  and  $250^\circ\text{C}$ . The results showed that fly ash was capable of adsorbing mercury. They also found that the adsorption capacity was related to temperature, mercury concentration,  $\text{NO}_x$

concentration, and HCl concentration in flue gas. They concluded that the adsorption capacity increased when the temperature decreased, the mercury concentration increased, the NO<sub>x</sub> concentration decreased, or the HCl concentration increased. Malerius and Werther, (2003) investigated mercury capture in an existing sewage sludge incineration plant. They found that the adsorption isotherm of fly ash was the Langmuir type whereas the adsorption isotherm of activated coals and zeolites were the Freundlich type.

A number of researches found that mercury capture often correlates directly with carbon content in residual fly ash (Hassett and Eylands, 1999; Huggins et al., 2000; Butz et al., 1999; Butz et al., 2000; Butz and Albiston, 2000; Hower et al., 2000a; Hower et al., 2000b). Serre and Silcox (2000) reported that unburnt carbon which remained in coal fly ash could be used as a low cost and effective replacement for activated carbon. Adsorbed-phase concentration was approximately 600 ppm. These results showed that a dilute suspension of fly ash in flue gas ducts and in baghouse filters could adsorb Hg<sup>0</sup> and that the best option for controlling Hg<sup>0</sup> emissions using fly ash appeared to be injection pulses prior to a baghouse filter. The effect of the porous structure and surface functionality on the mercury capture of fly ash carbon and its activated sample has also been investigated by Serre and Silcox (2000). They found that the activated fly ash carbon samples had lower mercury capacity than its preceding fly ash carbon (0.23 mg.g<sup>-1</sup> versus 1.85 mg.g<sup>-1</sup>), although its surface area was around 15 times larger, 863 m<sup>2</sup> g<sup>-1</sup> versus 53 m<sup>2</sup> g<sup>-1</sup>. Maroto-Valer et al. (2001) found that oxygen functionality and the presence of halogen species on the surface of fly ash carbons could promote mercury adsorption, whereas the surface area did not seem to have a significant effect on their mercury adsorption capacity. Bannerjee et al. (2005) found that adsorption efficiency depended on the initial concentration with adsorption behavior following the Langmuir adsorption model (up to a maximum adsorption capacity for Hg (II) of 11.00 mg g<sup>-1</sup> and the adsorption process was endothermic reaction.)

Isabel and Parra (2007) reported that the relationship between Hg capture and the percentage of carbon in fly ashes from the combustion of bituminous coal showed a high correlation ( $r^2 = 0.98$ ) and ( $r^2 = 0.82$ ) for anthracitic fly ash. Different types of unburnt carbons have an affect on the amount of adsorbed Hg. Maroto-Valer et al. (2001) reported

that for many ashes, the loss-on-ignition (LOI) content could equate the amount of unburnt carbon. Lu et al. (2007) found that mercury was mainly adsorbed on the unburnt carbon in fly ash. Hwang et al. (2002); Gustin and Ladwig (2004); and Xin et al. (2006) suggested that unburnt carbon had stronger adsorption strength toward mercury than other ash components. Therefore, high content of unburnt carbon may significantly contribute to the relatively low mercury released from fly ash.

## **2.9 Leachate of Mercury from fly ash**

Mercury adsorbed by fly ash has the potential to leach into water systems and thus possibly cause a problem of secondary environmental pollution. A number of researchers have found that the surface layer of fly ash probably contains some leachable materials (Prasad et al., 1996; Mohapatra and Rao, 2001; Iyer, 2002; and Reijnders, 2005), but they showed that in general heavy metals were poorly leached from fly ashes and the leaching extent was dependent on the chemical condition of the water system. The leachability from fly ash was dependent on the ratio of weight of spent adsorbent / leaching solution, pH of solution, concentration of the elements, temperature, pressure, and time. Prasad et al. (1996) found that rapid leaching of most of the trace metals except Cu into water, took place on the surface of ash particles at lower pH range 3.0 to 5.0 but elements in the leachate were within acceptable limits. The other important factors which relate mercury leaching are characteristics of fly ash such as loss-on-ignition (LOI), specific surface area, and total ammonia concentration (Wang et al., 2007). Wang et al., (2007) studied the role of ammonia on mercury leaching from coal fly ash. The results indicated that a very low concentration of mercury (less than  $150 \text{ ng.l}^{-1}$ ) was observed when deionised, deionised water was used as a leaching solution. They also found that increasing of ammonia concentration in leaching solution enhanced the mercury leaching in the alkaline pH range 9 to 10, due to the formation of less adsorbable mercury-ammonia complexes. Rio and Delebarre, (2003) reported that only 7% of mercuric ions adsorbed onto sulfo-calcic fly ash released into leaching solution when pH was fitted at 5.0 and 24 hours contact time, while approximately 16% of mercury released from Hg adsorbed onto silico-aluminous ash.

In conclusion, the review of source, of amount, and of physical and chemical properties of fly ash, has shown that fly ash has ability to utilise as low cost adsorbent material to adsorb many pollutants which contaminated in the environment, especially when using fly ash to adsorb heavy metals in both aqueous and flume gas. However, there are two limiting point of views that little done by the reviews. Firstly, many studies were done on optimum conditions suitable for removal of mercury such as contact time and adsorption capacity at low pH (3.0 to 5.0.) However, no work has been done on natural pH and temperature which are usually found in the environment. Secondly, there has been no work done to establish if fly ash has any potential to stabilise Hg under anaerobic condition with organic rich sediment at pH between 6.0 and 8.0 as occurs in the natural environment. Then, therefore, this investigation needs to focus on using fly ash to remove low concentration of Hg from freshwater under anaerobic conditions with organic rich sediment by adsorption process.

## Chapter 3

### Methodology

#### 3.1 Material

The fly ash used as the adsorbent in this study was obtained from the 4,000 Mwatt Ekibatuz Power Plant in Kazakhstan fired with high ash medium volatile coal. The chemical composition of the fly ash samples is shown in Table 3-1. The major chemical composition of the fly ash samples used in this study was silica, ( $\text{SiO}_2$ ), alumina, ( $\text{Al}_2\text{O}_3$ ), and ferric oxide, ( $\text{Fe}_2\text{O}_3$ ), which made approximately 74% by dry weight, and the main minor chemical components were approximately 2% calcium oxide ( $\text{CaO}$ ), and unburnt carbon, 18.06% (by dry weight) (Determined by using Elemental analyzer Flash EA1112 Series.) The result is shown in appendix A.



Table 3-1 Chemical composition of fly ash obtains from Ekibatuz fly ash, Kazakhstan

Constituent	wt%
Silica (SiO <sub>2</sub> )	47.9
Alumina (Al <sub>2</sub> O <sub>3</sub> )	24.2
Ferric oxide (Fe <sub>2</sub> O <sub>3</sub> )	1.89
Calcium oxide (CaO)	1.60
Magnesium oxide (MgO)	0.54
Sulfur trioxide (SO <sub>3</sub> )	0.32
Titanium dioxide (TiO <sub>2</sub> )	0.69
Potassium oxide (K <sub>2</sub> O)	0.73
Sodium oxide (Na <sub>2</sub> O)	0.42
Phosphorus pentaoxide (P <sub>2</sub> O <sub>5</sub> )	0.10
Unburnt Carbon	17.88*
other	3.73
Total	100.00

**Note: Tested by Department of Science Service, Ministry of Science Technology,**

**Thailand, using X-ray fluorescence spectrometer (Uniquant 2 software)**

**\* Tested by Elemental analyzer Flash EA112 Series**

The chemical composition of fly ash indicates that it is a Class F type ash. The fly ash composition is similar to the silico-aluminous fly ash which was used in a study of removal of mercury in aqueous solution by fluidized bed plant fly ash by Rio and Delebarre, (2003). However, the unburnt carbon content in silico-aluminous fly ash of Rio and Delebarre was very low (below  $0.5 \times 10^{-3} \text{ mg.g}^{-1}$ ), while the unburnt carbon content in the fly ash used in this study was 18.06 percent ( $180 \text{ mg.g}^{-1}$ ).

Table 3-1 shows that fly ash used in this study had a high unburnt carbon content. Hasset and Eylands (1999) stated that carbon was thought to play a significant role in Hg capture on fly ash. Xin et al. (2006) noted that loss-on-ignition was normally used as an indicator of unburnt carbon content in fly ash. In this study loss-on-ignition was also used to determine carbon content. The sufficient amount of fly ash was dried for 24 h at 105°C to remove water. 5 g of dried ash was placed in a crucible and heated for 3 hours at 850°C before placing in a desiccator (See Appendix A).

### **3.2 Method**

#### **3.2.1 Sample preparation**

##### **A) Determination of Hg in solution**

##### **Reagents and Standards**

Reagents may contain mercury as an impurity. For high sensitivity uses ultra-pure reagents.

##### **1. Water,**

For all sample preparations and dilutions distilled or de-ionised, DI water is required.

##### **2. 0.2 N (0.0333 mol l<sup>-1</sup>) Potassium Bromate (KBrO<sub>3</sub>).**

Dissolve 1.39 g potassium bromate (BDH Anala R.: KBrO<sub>3</sub> = 167.01 g.mol<sup>-1</sup>) in 250 ml water. Prepare weekly.

##### **3. 0.2 N (0.2 mol l<sup>-1</sup>) Potassium Bromide (KBr).**

Dissolve 5.95 g potassium bromide (BDH Anala R.: KBr = 119.01 g.mol<sup>-1</sup>) in 250 ml water. Prepare monthly.

##### **4. 0.1 N Potassium Bromide-0.1 N Potassium Bromate.**

Mix equal volume of 0.2 N potassium bromate and 0.2 N potassium bromide. A total volume of 200 ml will allow digestion for 100 samples. Prepare daily.

##### **5. 1.73 mol (12% m/v) Hydroxylamine hydrochloride (OHNH<sub>3</sub>Cl).**

Dissolve 12 g of high purity hydroxylamine hydrochloride (BDH Anala R.: OHNH<sub>3</sub>Cl = 69.49 g.mol<sup>-1</sup>) in approximately 80 ml water and dilute to 100 ml in volumetric flask. Prepare weekly.

6. 10 mmol (33% v/v) Hydrochloric Acid (HCl).

Dilute 167 ml of high purity 9.78 mol (36% m/m) hydrochloric acid (Fisher Scientific Laboratory reagent grade: Specific Gravity, S.G.1.18 (36%)) to 500 ml with DI water.

7. 0.443 mol (2% m/v) Tin (II) Chloride ( $\text{SnCl}_2$ ).

Add 10 g of tin (II) chloride dehydrate (BDH Anala R.:  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O} = 225.63 \text{ g} \cdot \text{mol}^{-1}$ ) to 500 ml of 3.24 mmol (10% v/v) HCl (50 ml of HCl; Fisher Scientific Laboratory reagent grade: Specific Gravity, S.G.1.18 (36%)) dilute to 500 ml in volumetric flask with DI water), heat to dissolve if necessary. To remove any traces of mercury, bubble the solution with argon at a flow of 2 l per minute for 15 minutes (Note: the hydrochloric acid use to prepare this solution can be analytical grade since any mercury present will be removed on bubbling).

8. Reagent Blank.

For each 100 ml, prepare a solution containing 15 ml 10 mmol hydrochloric acid and 2 ml 0.1 N potassium bromate/potassium bromide per 100 ml. Add 30  $\mu\text{l}$  of 1.73 mol hydroxylamine hydrochloride for each 100 ml prepared.

**Note:** On the continuous flow system, the reagent blank solution is run as background for automatic blank subtraction. This solution may contain trace levels of detectable of mercury. It is important that the same reagents use for sample and standard preparation are used for preparation of the reagent blank.

8. Standard Mercury Solutions.

8.1 Calibration Standard Solution (Solution A-1000  $\text{mg l}^{-1}\text{Hg}$ .)

Mercury solution 1000  $\text{mg} \cdot \text{l}^{-1}$  in 1.59 mmol (10%) nitric acid (Fisher Scientific)

8.2 Solution B-10  $\text{mg l}^{-1}\text{Hg}$

Dilute 5 ml of solution A with DI water to approximately 100 ml. Add 10 ml of 0.1 N potassium bromate/potassium bromide, 75 ml of 10 mmol hydrochloric acid, 150  $\mu\text{l}$  of 1.73 mol hydroxylamine hydrochloride and dilute to 500 ml in borosilicate volumetric flask with water. Prepare weekly.

8.3 Calibration Standards.

Prepare a minimum of four mercury calibration standards spanning the concentration range of interest by serial dilution of stock solution B. Each calibration standard should contain 15 ml of 10 mmol hydrochloric acid, 2 ml of 0.1 N potassium bromate/potassium bromide

and 30  $\mu\text{l}$  of 1.73 mol hydroxylamine hydrochloride per 100 ml in borosilicate volumetric flask. Plastic flasks must not use as they are permeable to mercury (0) vapour. Prepare daily.

**Note:** The reagent blank solution is identical to the standard blank solution.

### **General Sample Preparation Procedure**

Accurate aliquots of the samples (30-40 ml) were pipetted into 50 ml tared containers. 7.5 ml of 10 mmol hydrochloric acid and 1 ml 0.1N potassium bromate/potassium bromide reagent were added to the sample and the vessel closed. The mixture was allowed to stand for at least 30 minutes. If a yellow coloration, due to free bromine, did not persist after 30 minutes or during storage, a further 1 ml of 0.1N potassium bromate/potassium bromide reagent was added. After at least 30 minutes 30  $\mu\text{l}$  of 1.73 mol hydroxylamine hydrochloride was added to remove excess bromine, indicated by the disappearance of the yellow colour from the sample. The sample was made up to 50 ml with deionised water and total Hg content was determined by an analytical procedure described in section 3.2.2. Two sub-samples were analysed for each experimental sample. Blanks were prepared at the same time using the same amounts of reagents and analysed along with the corresponding sample. Two sub samples were taken for an analysis and the average taken as the result.

### **B) Determination of Hg in ash**

Ash for the analysis was prepared following the P S Analytical's application note 069: "Determination of Mercury in Incineration Ash". This is based on USEPA methods 29 and 101A, together with ASTM Method D6784-02 (Ontario Hydro). 0.1 g of dry sample was put into a test tube. 6 ml of 11.11 mol  $\text{HNO}_3$  (Trace analysis grade: Nitric acid S.G. 1.42 (70%), Fisher Scientific) and 2 ml of 9.78 mol  $\text{HCl}$  (Laboratory reagent grade: Hydrochloric acid S.G. 1.18 (36%), Fisher Scientific) were added to the test tube. The mixture was refluxed at  $140^\circ\text{C}$  for 1.5 hours. Once cooled the sample was filtered through a 0.45  $\mu\text{m}$  cellulose nitrate membrane filter (Whatman 0.45  $\mu\text{m}$ .) The solution was made up to 100 ml with DI water. Duplicate samples were analysed for total Hg.

### 3.2.2 Analysis of Hg

After digestion, total mercury ( $\text{Hg}^{2+}$ ) in the extract was reduced to  $\text{Hg}^0$  by using 0.443 mol.  $\text{SnCl}_2$  in 3.24 mmol HCl (Laboratory reagent grade: Hydrochloric acid S.G. 1.18 (36%), Fisher Scientific).  $\text{Hg}^0$  was measured by cold vapour atomic fluorescence spectrometer (CVAFS), using the PSA 10.025 Millennium Merlin system following the analytical procedure developed by PSA Co., Ltd: (based on USEPA Method 1631, Revision C: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapour Atomic Fluorescence Spectrometry).

### 3.2.3 Adsorption of Hg onto PET bottle

In this study 500 ml Coke bottles were used as low cost PET bottle for reaction vessel. Polyethylene terephthalate (PET), Coke bottles were used as reaction vessels because of their low cost and very low mercury adsorbed characteristic (Copeland et al., 1996; Pedro and Wilson, 2000.) Mercury adsorption properties of Coke bottles were determined prior to the start of the experiment. Four replicate of bottles were filled with a solution of  $\text{HgCl}_2$  (0.424 nmol ( $0.0001 \text{ mg.l}^{-1}$ ) and  $2.12 \times 10^5$  nmol ( $50 \text{ mg.l}^{-1}$ ) and shaken at  $30^\circ\text{C}$  in the rate of 150 rpm for 96 hours. The control experiments were determined in parallel using four bottles contained deionised water. The average concentrations of total mercury in solution before shaking were 0,  $0.0001 \text{ mg.l}^{-1}$  and  $56.48 \text{ mg.l}^{-1}$ , respectively. The average results of total mercury solution after shaking for 96 hours were 0,  $0.0001 \text{ mg.l}^{-1}$  and  $55.68 \text{ mg.l}^{-1}$ , respectively. There was no significant adsorption at  $0.0001 \text{ mg.l}^{-1}$ , and only 1.4% was adsorbed at  $56.48 \text{ mg.l}^{-1}$  and this change was not consider significant. The student's t-test was used to compare the means of mercury concentrations between before and after adsorption process. The t-test illustrated no difference in mercury concentrations between before and after adsorption reaction. (See Appendix B) The result indicated that there were no mercury adsorptions onto reaction vessels.

### 3.2.4 Establishment of adsorption equilibrium time

0.025 g of fly ash and 100 ml of deionised water containing  $500 \mu\text{g Hg l}^{-1}$  were placed into a 500 ml polyethylene terephthalate (PET) bottle and stopped. Triplicate sample bottles

were then placed in an orbital shaker at 150 rpm and 30°C, and were shaken for different periods of time, from 24, 48, 72, 96, 120, 144 and 168 hours. After shaking, triplicate samples were removed and filtrated through cellulose nitrate membrane filters (Whatman: pore size 0.45µm). The filtered were prepared for determination of total Hg in liquid sample following the procedure in section 3.2.1 A.

The resulting equilibrium mercury concentrations in solution were used to calculate adsorption isotherms. The adsorbent phase concentration after equilibrium was computed by Eq.3-1.

$$\frac{X}{M} = \frac{(C_o - C_e)V}{m} \quad 3.1 \text{ (George et al., 2003)}$$

Where  $\frac{X}{M}$  = adsorbent (i.e., solid) phase concentration after equilibrium, mg adsorbate g<sup>-1</sup> adsorbent

$C_o$  = initial concentration of adsorbate, mg.l<sup>-1</sup> in solution

$C_e$  = final equilibrium concentration of adsorbate in solution after adsorption has occurred, mg.l<sup>-1</sup>

$V$  = volume of liquid in the reactor, L

$m$  = mass of adsorbent, g

Mercury uptake was plotted against time to establish the minimum time to react mercury adsorption equilibrium between Hg on fly ash and solution. The time at maximum mercury uptake was used as the contact time for all adsorption isotherm experiments as described below.

### 3.2.5 Adsorption isotherm determination

#### 3.2.5.1 Effect of pH on adsorption isotherm of Hg onto fly ash at different concentrations

The experimental design consisted of 4 mercury concentrations; 0.0 (control), 5.0, 10, 50, and 100 mg.l<sup>-1</sup>. 3 replicates were prepared for each set. 1 g of air dried ash was placed in a washed and dried 500 ml PET bottle, and 100 ml of experimental Hg solution added to each. 1 M NaOH or 1 M HCl was added to the mixture to adjust pH of 6.0, 7.0 and 8.0 (the total volume of 1 M NaOH and 1 M HCl added was recorded for calculation of final concentration.) Samples were shaken at 150 rpm and 30°C for 96 hours. The samples were filtered through cellulose nitrate membrane filters (Whatman: pore size 0.45 µm) and total Hg was determined.

The mercury uptake (X/M) was plotted against final concentration (C<sub>e</sub>) in solution to evaluate the adsorption isotherms.

The effect of pH on adsorption isotherm was studied using the data of the mercury uptake (X/M) from mercury concentration 5.0, 10.0, 50.0 and 100 mg.l<sup>-1</sup>. A log of mercury uptake (X/M) was plotted against a log of final concentrations (C<sub>e</sub>) in solution to evaluate uptake using the Freundlich isotherm. (See results in Appendix C).

The Freundlich equation was used to describe relationship between the adsorption of solutes from a liquid and solid surface. The Freundlich equation is:

$$\frac{X}{M} = K_f C_e^{1/n} \quad 3.2 \text{ (George et al., 2003)}$$

Where  $\frac{X}{M}$  = mass of adsorbate adsorbed per unit of adsorbent, mg adsorbate g<sup>-1</sup> fly ash,

$K_f$  = Freundlich capacity factor, (mg adsorbate g<sup>-1</sup> fly ash) (l water mg<sup>-1</sup> adsorbate)<sup>1/n</sup>

$C_e$  = equilibrium concentration of adsorbate in solution after adsorption, mg.l<sup>-1</sup>

$1/n$  = Freundlich intensity parameter

### **3.2.5.2 Effect of adsorbent to solute ratio on Mercury removal**

6 concentrations of air dried fly ash 0.0 (control), 0.1, 0.2, 0.5, 1.0, 2.0 and 3.0 g and samples were placed into washed and dried 500 ml PET bottles, and 100 ml of 1.5 mg.Hg l<sup>-1</sup> was added to each bottle. 1 M NaOH or 1 M HCl was added to the mixtures to adjust the pH to 6.0, 7.0 and 8.0 (the total volume of 1 M NaOH and 1 M HCl added was record to allow adjustment for calculated of volume of leachate.) The 3 replicates were shaken at 150 rpm and 30°C for 96 hours. The samples were filtered through cellulose nitrate membrane filters (Whatman: pore size 0.45 µm) and total Hg was determined.

The mercury uptake (X/M) was plotted against final concentration (C<sub>e</sub>) in solution to evaluate the adsorption isotherm.

### **3.2.6 Establishment of desorption equilibrium time**

Desorption of Hg<sup>++</sup> from fly ash was studied using 10 g of fly ash placed in a 2 l flask containing 1000 ml of 50 mg.Hg l<sup>-1</sup>. The mixture was shaken for 96 hours to achieve equilibrium. The mixture was filtered through a cellulose nitrate membrane filter (Whatman: pore size 0.45µm.) The moisture content of the residual wet Hg-load ash was analysed by weighing 1 g of the wet ash in a porcelain basin and putting into an oven at 105°C for 2 hours. The samples were cooled in a desiccator and weighed. The same step was repeated until the weight of sample remained constant. The adsorbed Hg concentration of wet ash and air dried Hg-loaded ash were determined by following the procedure of determination of total mercury using PSA 10.025 Millennium Merlin methodology for sludge and soil.

#### **3.2.6.1 Desorption from wet fly ash**

A 1 g (d.w.) sample of Hg loaded wet fly ash containing 3.0 mg.Hg g<sup>-1</sup> and 100 ml of DI water was placed in PET bottles. The mixture was allowed to equilibrate for 24, 48, 72 and 96 hours on a shaker at 150 rpm and filtered through cellulose nitrate membrane filters



(Whatman: pore size 0.45 $\mu\text{m}$ .) The concentration of mercury desorbed was determined from the filtrate solution (Voudrias et al., 2002).

### **3.2.6.2 Desorption from air dried fly ash**

A sample of the fly ash that had come into equilibrium with the mercury solution was allowed to air dry. The 1 g (d.w.) sub-sample of air dried Hg-loaded ash containing 3.0 mg.Hg g<sup>-1</sup> was used instead of wet ash for comparison purposes. Mercury adsorption was plotted against time for both wet ash and air dried ash loaded with Hg. 3 replicates were used.

### **3.2.6.3 Effect of Mercury loaded wet fly Ash on Mercury leachate**

Three sets of experiments were designed for desorption isotherm. Each set consisted of Hg loaded wet fly ash; 0.0 (control), 0.085, 0.17, 0.34, and 1.7 g (d.w.) which contained 0.00, 0.26, 0.54, 1.08, and 5.3 mg.Hg g<sup>-1</sup> (d.w.), respectively. The 3 replicates of Hg loaded wet fly ash were put into washed and dried 500 ml PET bottles, and 100 ml deionised water was added to each bottle. The samples were adjusted to pH 6.0, 7.0 and 8.0 with 1 M NaOH or 1 M HCl. The total volume of 1 M NaOH and 1 M HCl used were recorded. The 3 replicates were shaken at 150 rpm and 30° C for 96 hours. Total Hg was determined by procedures described in section 3.2.1 A and 3.2.2. Mercury concentrations in solution and mercury loaded were plotted for desorption isotherm.

### **3.2.7 Stability of adsorbed Mercury on coal-fired power plant fly ash in anaerobic organic rich conditions**

This experiment was designed to test whether fly ash could immobilise Hg in organic rich anaerobic condition, which would cause consequently reduce biological mercury methylation.

#### **3.2.7.1 Collection and preparation of sediment**

Preparation of sediment: Sediment rich organic matter was taken from a small reservoir (approximately 4 ha) at Leominstead on Bartly water stream in the New Forest (Southern England) in March 2008 (O.S. 4278, 1094.) The reservoir is fed by a small stream, which

drains a rural area. The pH of the overlying water was 5.8 to 6.0. The unpolluted sediment from Bartley brook reservoir was prepared by wet-sieved through a 3.0 mm mesh size sieve to remove large materials. Fresh garden compost and macerate were also sieved through 3.0 mm mesh size. The sediment and fresh garden compost were put into a glass container, and kept at 4°C to conserve a constant composition during the experimental period.

### **3.2.7.2 Determination of the ability of power station fly ash to immobilise Mercury in anaerobic rich organic sediments.**

4 stock solutions were prepared for each treatment:

1) **Control A** had no mercury or fly ash added.

400 ml of deionised water was added into a 1 l flask followed by the wet sediment (containing 47.5 g of sieved sediment dry weight) and 2.5 g (dry weight) of garden compost, giving a ratio of (90:9.5:0.5). The mixture was made up to 500 ml with DI water.

2) **Control B** was the same as Control A in all respects except that ml of a 9.5 ml of 1 mg.ml<sup>-1</sup> stock solution mercuric chloride, was added. This gave a Hg concentration of 200 mg.Hg kg<sup>-1</sup> of sediment.

3) **Treatment A:** same preparation as Control B but with 0.5 g fly ash added.

4) **Treatment B:** same preparation as Control B but with 3.0 g fly ash added.

The flasks were flushed with oxygen free nitrogen gas (N<sub>2</sub>) and stirred for 30 minutes.

A 100 ml subsample of each was taken, filtered, and the amount of Hg in solution measured. 4 samples of 100 ml of each solution were placed into 150 ml flasks, flushed with N<sub>2</sub> to expel air and stoppered.

The samples were placed into a shaking incubator at 100 rpm and 30°C for 8 weeks. After 8 weeks the samples were filtered through cellulose nitrate membrane filter paper (pore size 0.45µm.) The pH was measured prior to the Hg analysis. For samples that were not

analysed immediately, 4 ml of 4 M HCl was added to stabilise the supernatant, and then stored in an airtight glass vial below 5°C.

### **3.2.7.3 Determination of the importance of unburnt carbon in fly ash and its ability to immobilise Mercury in anaerobic rich organic sediments.**

These experiments were repeated exactly like the ones above, exactly that the ash used had been heated at 850°C for 3 hours in air to remove unburnt carbon as previously described in 3.1.2.

### **3.3 Quality Assurance**

The quality assurance procedure in this study followed the CITAC/EURACHEM GUIDE: Guide to Quality in Analytical Chemistry (The Cooperation on International Traceability in Analytical Chemistry and A Focus for Analytical Chemistry in Europe, 2002). The accepted criteria in this study are given below:

- a) The working range of the CVAFS Hg determination was approximately 1 ng.l<sup>-1</sup> (ppt) to 100 µg.l<sup>-1</sup> (ppb). If mercury concentrations were higher than working range, the samples were diluted prior to the analysis.
- b) A method detection limit (MDL) was obtainable less than 1 ng.l<sup>-1</sup> when using the high purity reagents.
- c) The mercury concentration in reagent blank was less than 0.1 µg.l<sup>-1</sup>.
- d) The relative standard deviation (RSD) was less than 15% for concentrations greater than twenty times MDL. (See below)
- e) The accuracy (% recovery) for a known mercury standard solution was between 80 and 120 percent.

### 3.3.1 Determination of detection limit of Hg

The precision of the procedure described in the methodology in section 3.2.1 and 3.2.2 for measuring mercury was determined by spiking 10 samples of reagent blank; for Hg determination in solution using DI water and using a mixture of 6 ml of HNO<sub>3</sub> (Trace analysis grade: Nitric acid S.G. 1.42 (70%), Fisher Scientific) and 2 ml of HCl (Laboratory reagent grade: Hydrochloric acid S.G. 1.18 (36%), Fisher Scientific) for Hg determination in fly ash, with 5 ng.l<sup>-1</sup> of Hg prior to the analysis.

The MDL of both liquid and solid samples were computed by using equation 3.3

$$\text{MDL} = t_{(n-1, 1-\alpha = 0.99)} (S) \quad (3.3)$$

Where: MDL = the method detection limit

$t_{(n-1, 1-\alpha = 0.99)}$  = the student's t value appropriate for a 99% confidence level and a standard deviation estimated with n-1 degrees of freedom.

S = standard deviation of the replicate analyses.

#### A) Method detection limit of water determination

The results of ten replicate samples of spiked water were 5.480, 5.157, 5.800, 5.272, 4.824, 4.763, 5.580, 5.532, 5.163 and 5.348 ng.l<sup>-1</sup>, respectively. The standard deviation was  $\pm 0.329$  and the MDL was 1.0 ng.l<sup>-1</sup>.

#### B) Method detection limit of fly ash determination

The method of determining the precision of the amount of Hg in mixture of aqua regia (3:1 HCl:HNO<sub>3</sub>) is used to digest fly ash in samples. The results of ten replicate spiked samples which were shown to contained the following amount Hg: 5.751, 5.789, 5.892, 5.54, 5.749, 5.858, 5.188, 5.041, 5.216 and 5.334 ng.l<sup>-1</sup>, respectively. The standard deviation was  $\pm 0.288$  and method detection limit for fly ash was 1.0 ng.l<sup>-1</sup>.

### 3.3.2 Precision and accuracy study

In this study, the precision, (% RSD) and accuracy, (% recovery) were expressed using equation 3.4 and 3.5, respectively. The % RSD of the reported results were not more than 15% and % recovery of quality control standard was between 80 and 120 percent.

$$\text{Precision, (\% RSD)} = \frac{S}{X_{ave}} \times 100 \quad (3.4)$$

$$\text{Accuracy, (Ave. \% Recovery)} = (X_{ave}/\text{spike level}) \times 100\% \quad (3.5)$$

Where S = Standard deviation

$X_{ave}$  = Average Hg concentration

### 3.3.3 Determination of total Hg in reference material

Quality assurance for determination of total Hg in solid reference material sample was determined. Triplicate samples of natural matrix certified reference sewage sludge; (CRM CNS311-04-050) was digested following P S Analytical's application note 069 and using the PSA 10.025 Millennium Merlin system. Table 3-2 shows the certified concentrations in  $\text{mg.kg}^{-1}$  (parts per million). The results of total Hg in CRM determination was presented in table 3-3. The average measured concentration of Hg was a little higher than in the reference value. However, the test result was within the confidence interval (1.20-2.23  $\text{mg.kg}^{-1}$ ). The interval of test result of Hg concentration was 0.3  $\text{mg.kg}^{-1}$  or 19% when compared with reference value. However, the precision and accuracy of CRM determination were 3.03% and 119%, respectively. This indicated that the precision and accuracy were within acceptable criteria.

**Table 3-2 Certified analyte concentrations**

Element	Reference Value	S.D	Confidence Interval	Prediction Interval
<b>Mercury, Hg</b>	<b>1.71</b>	<b>0.828</b>	<b>1.20-2.23</b>	<b>0.00-3.61</b>

**Table 3-3 The results of total Hg in CRM**

Sample ID	Total Hg concentration, mg.kg <sup>-1</sup>	S.D	Standard error
A	2.108	0.0618	0.0357
B	2.013		
C	1.992		
Average	<b>2.038</b>		

## Chapter 4

### Mercury adsorption-desorption onto coal-fired fly ash

#### 4.1 Establishment of adsorption equilibrium time of Mercury onto power station fly ash

An equilibration was achieved between uptake of mercury onto fly ash from a solution of  $0.5 \text{ mg l}^{-1}$  mercury as mercury chloride after 96 hours at pH 7.0 (see Figure 4-1 and Figure 4-2). 96 hours was therefore taken as the minimum equilibrium time in all adsorption experiments as described in this thesis.

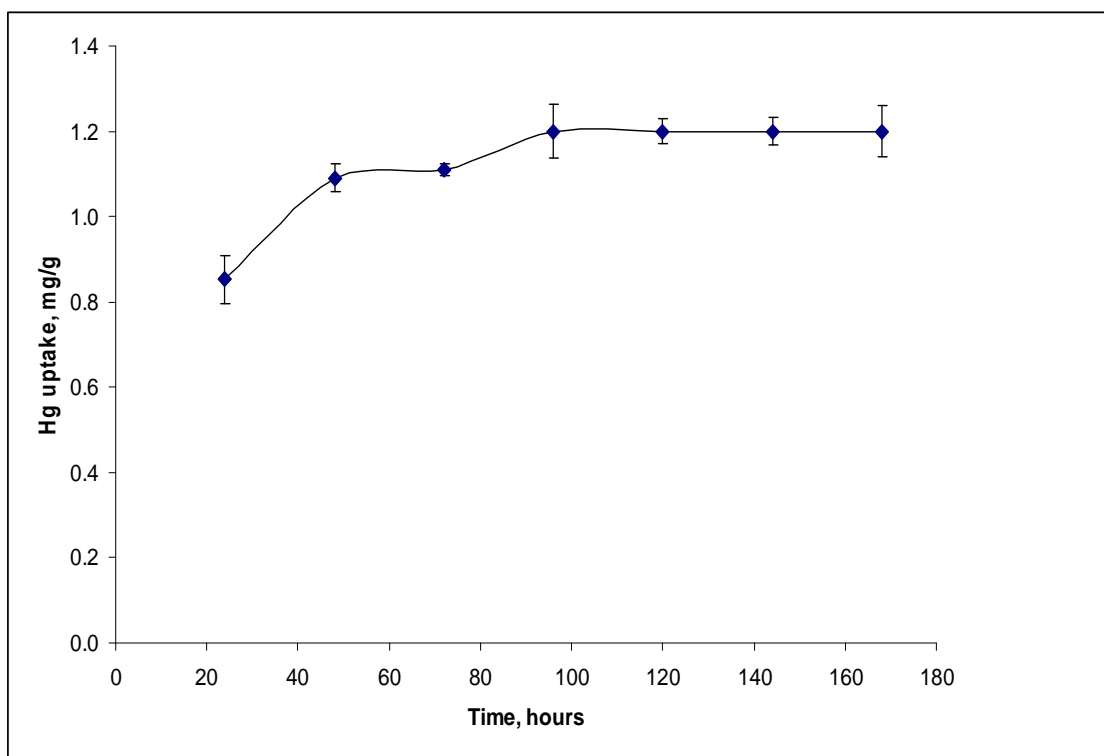
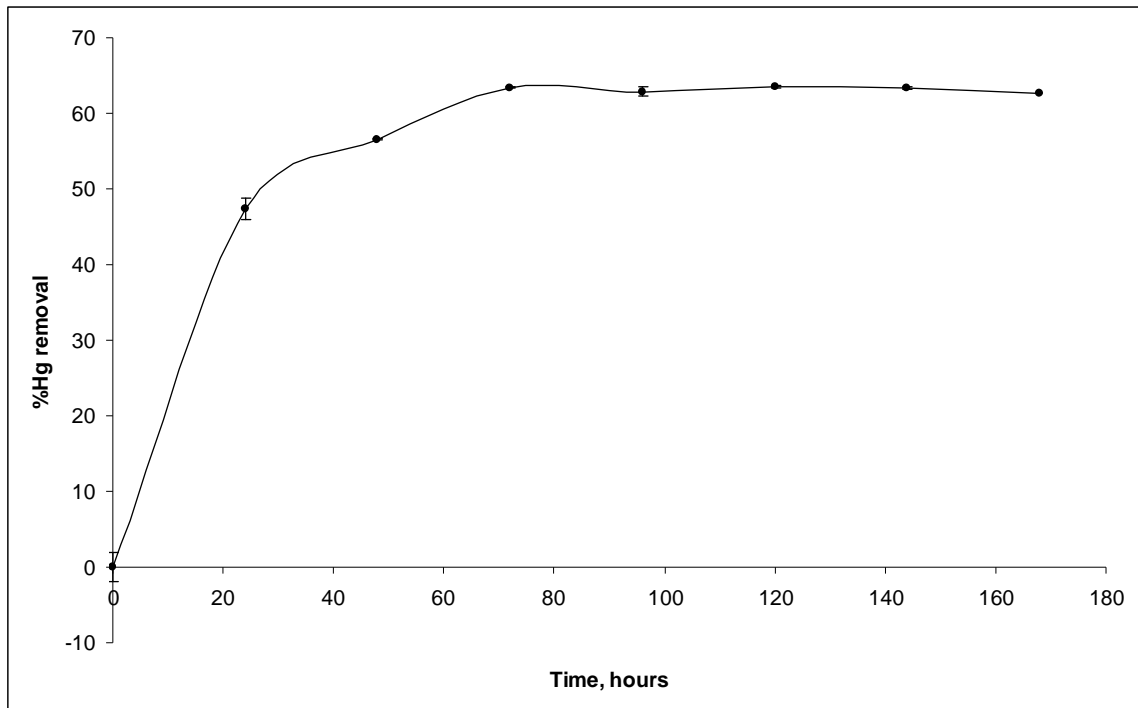


Figure 4-1 Equilibrium time for the adsorption of Hg from 100 ml solution of  $0.5 \text{ mg l}^{-1}$  of mercury onto 0.025 g of fly ash at pH 7.0



**Figure 4-2 Percent Hg removal at equilibrium time from 100 ml solution of  $0.5 \text{ mg l}^{-1}$  of mercury onto 0.025 g of fly ash at pH 7.0**

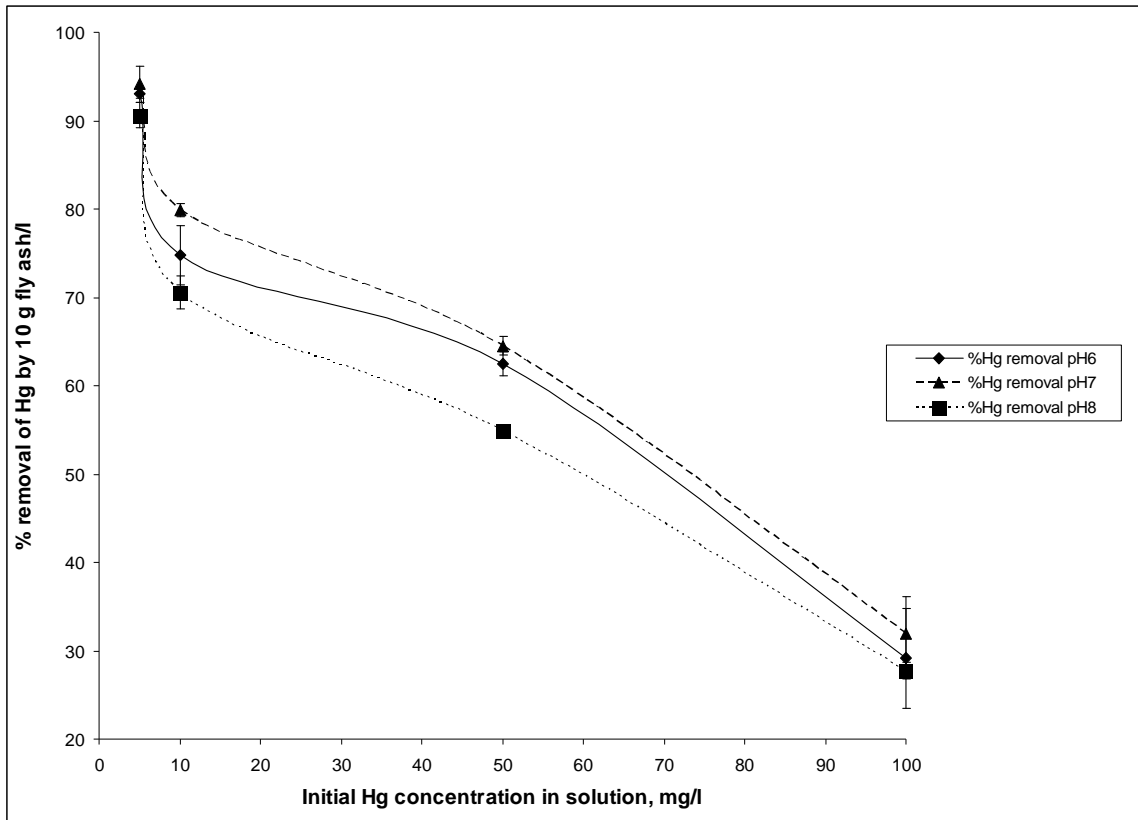
## **4.2 Effect of pH on adsorption isotherm of Hg onto fly Ash at different concentrations**

### **Introduction**

This experiment investigates the effect that levels of acidity and alkalinity found in natural water system might have on the ability of fly ash to adsorb mercury.

Figure 4.3 shows the effect of initial Hg concentration in solution on Hg adsorbed onto fly ash at pH 6.0, 7.0 and 8.0. At low concentration ( $5 \text{ mg l}^{-1}$ ),  $10 \text{ g l}^{-1}$  of fly ash were capable of removing approximately 92% of Hg from solution at pH 6.0 to 8.0, but the amount adsorbed dropped rapidly when the concentration was raised to  $10 \text{ mg l}^{-1}$ , and then steadily dropped to approximately 30% removal when the concentration was  $100 \text{ mg l}^{-1}$  of Hg in solution. Most Hg was adsorbed at pH 7 and least at pH 8 but the maximum difference was only 10%.





**Figure 4-3 Effect of initial Hg concentration on Hg adsorbed onto 10 g of fly ash at three pHs, from 1 l of Hg solution**

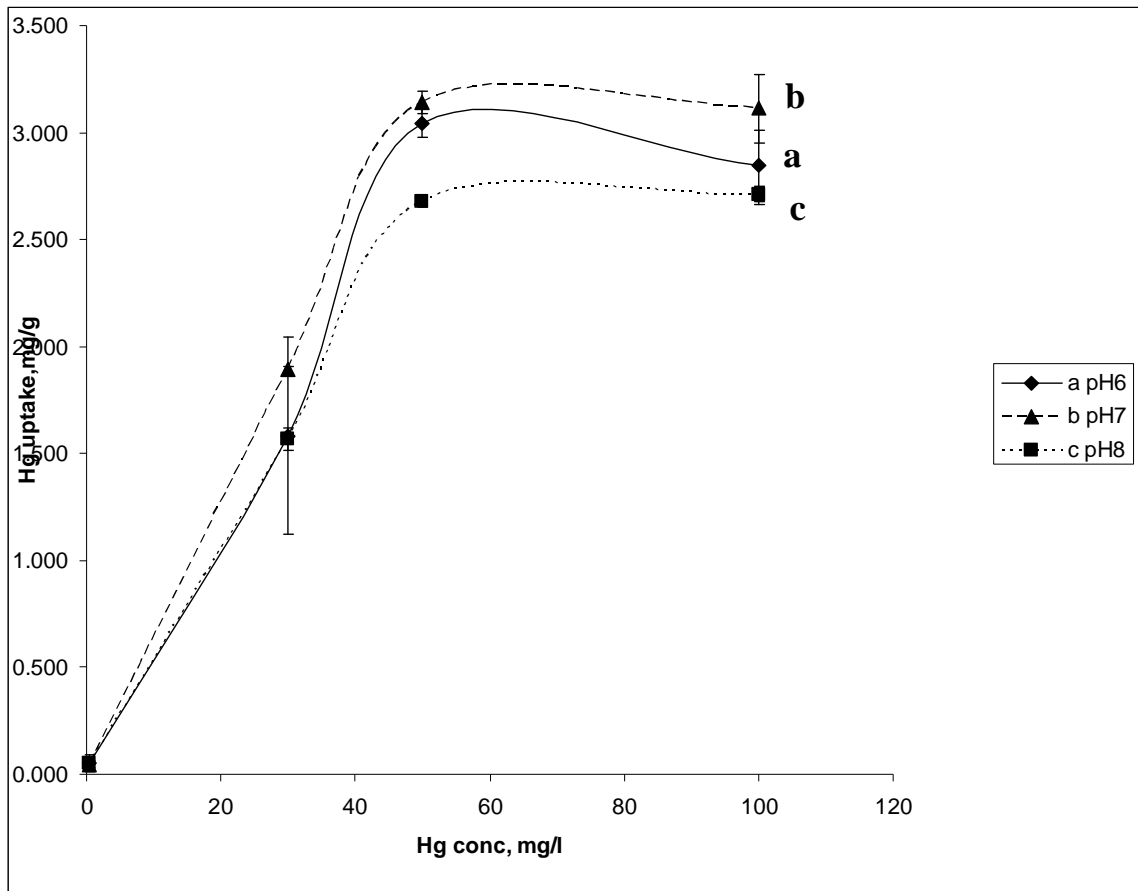
The data from Figure 4.4 expresses a mercury uptake in  $\text{mg g}^{-1}$  fly ash at different concentrations of Hg in solution, in order to explain the nature of the adsorption curve. The graph clearly shows that the maximum amount of Hg that fly ash can adsorb is  $3 \text{ mg g}^{-1}$  from a solution containing  $50 \text{ mg l}^{-1}$  Hg. Fig.4.4 confirmed the finding that the maximum capacity of Ekibatuz fly ash was 3 % of Hg taken up from a solution of  $100 \text{ mg l}^{-1}$ .

The adsorption isotherm for the uptake of Hg from 1 l of solution containing up to  $50 \text{ mg l}^{-1}$  by  $10 \text{ g l}^{-1}$  of fly ash was:

pH 6 isotherm a

pH 7 isotherm b

pH 8 isotherm c

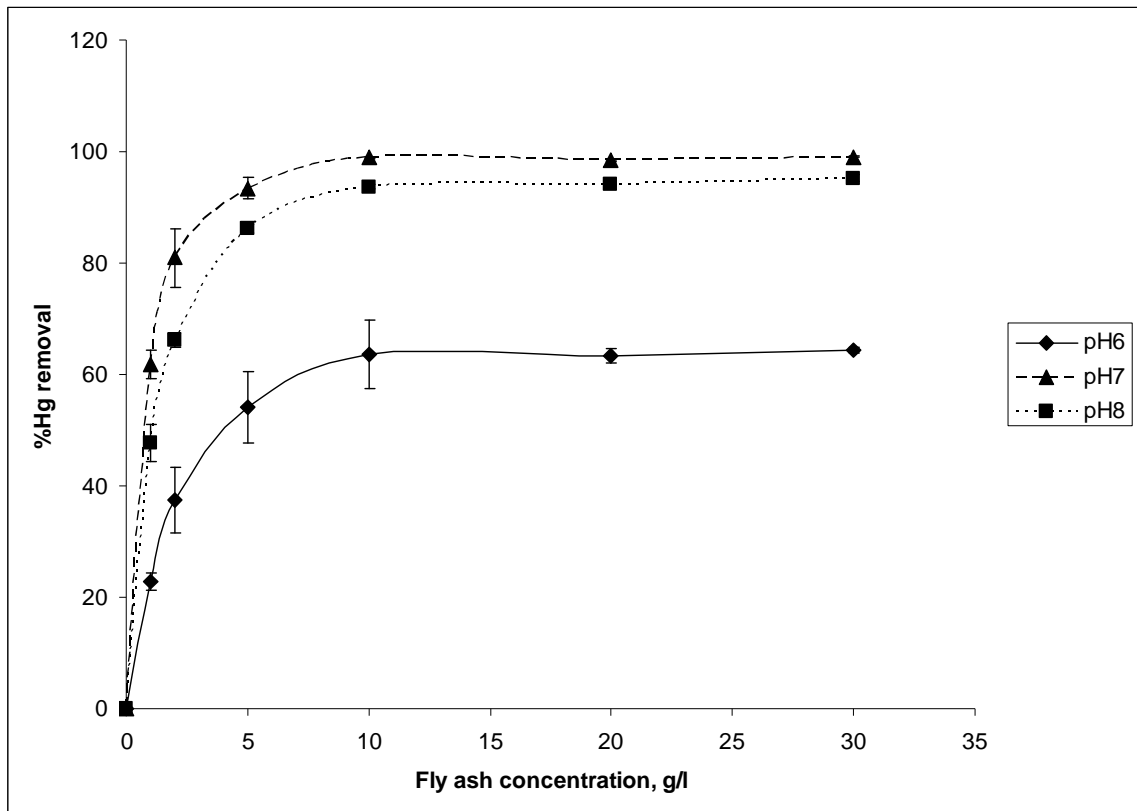


**Figure 4-4 Uptake of Hg on 10 g fly ash from different initial Hg concentration in 1 l of solution at three pHs**

#### **4.3 Effect of adsorbent to solute ratio on Mercury removal at pH 6, 7 and 8**

The percentage of mercury removal from 1 l of solution containing  $1.5 \text{ mg l}^{-1}$  of Hg with different quantities of ash at pH 6, 7 and 8 is shown in Figure 4.5. Maximum uptake of Hg occurred when  $10 \text{ g l}^{-1}$  of ash had been added to the mercury solution. At pH 7 some 98.9% was adsorbed and falling to 93.7% at pH 8, but at pH 6 only 63.6% was adsorbed.

In all further studies undertaken the maximum concentration of fly ash was  $10 \text{ g l}^{-1}$ .

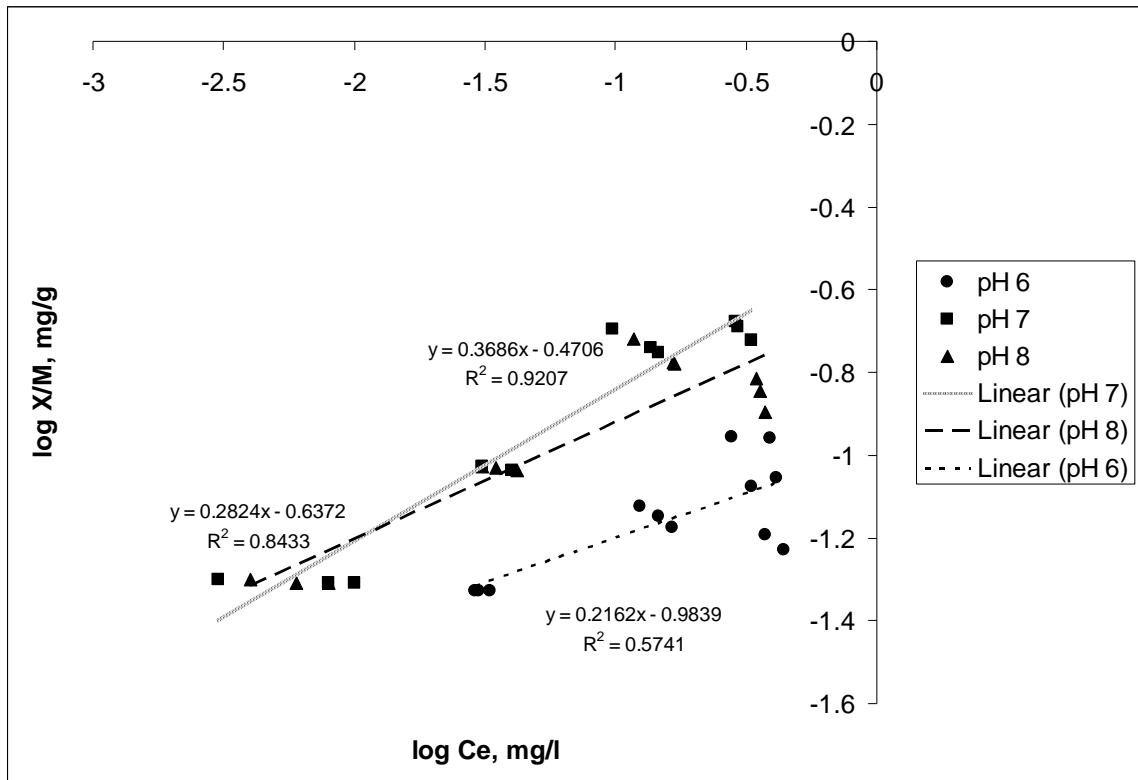


**Figure 4-5 Effect of fly ash dosage on %Hg removal at 1.5 mg l<sup>-1</sup> of initial Hg concentrations**

The Freundlich adsorption isotherms for the above experiment are given in Table 4-1. (For calculation see Appendix C) The isotherm was devised from the uptake curve up to the point that maximum adsorption was reached (ie. 10 g l<sup>-1</sup> fly ash.) The quantity of mercury sorbed in g g<sup>-1</sup> of adsorbent for a unit equilibrium concentration of the Hg, K, and the sorption intensity (*n*), after 96 hours were calculated and shown in Table 4-1. The R<sup>2</sup> are very high confirming that the Freundlich isotherm is the correct equation to use to express the uptake of Hg onto power station fly ash. This supports the finding of Grover and Narayanswamy, (1982); Kapoor and Viraraghavan, (1992); and Viraraghavan and Dromamraju, (1991).

**Table 4-1 The Freundlich isotherm for the adsorption of Hg from ash at pH 6, 7 and 8 at different concentration of equilibrium solution**

pH of initial solution	Freundlich equation	K	<i>n</i>	R <sup>2</sup>
6.0	$X/M = 0.104C^{1/0.608}$	0.104	0.608	R <sup>2</sup> =0.574
7.0	$X/M = 0.338C^{1/0.426}$	0.338	0.426	R <sup>2</sup> =0.921
8.0	$X/M = 0.231C^{1/0.522}$	0.231	0.522	R <sup>2</sup> =0.843



**Figure 4-6 Equilibrium isotherm (Freundlich) of mercury uptake onto fly ash from different fly ash concentrations and 500  $\mu\text{g. l}^{-1}$  of  $\text{HgCl}_2$  solution at pH 6, 7 and 8**

## 4.4 Desorption isotherm

### 4.4.1 Establishment of desorption equilibrium time

10 g of fly ash containing  $3 \text{ mg g}^{-1}$  of Hg was placed into 1 l of deionised water and allowed to come into equilibrium. Figure 4-7 shows the time to equilibrium for both wet and air dried fly ash. Desorption equilibrium was achieved after 96 hours at pH 7.0 ( $30^\circ\text{C}$ ). The amount of total mercury in solution was determined using the procedure described in 3.2.1 A and the amount of mercury adsorbed onto fly ash was determined using the procedure described in 3.2.1 B. Figure 4-8 shows that desorption equilibrium was achieved after 48 hours with approximately 6% of Hg being desorbed from the air dried ash and 12% from wet ash. The result shows that mercury on air dried ash tends to be more tightly bound than mercury on wet ash.

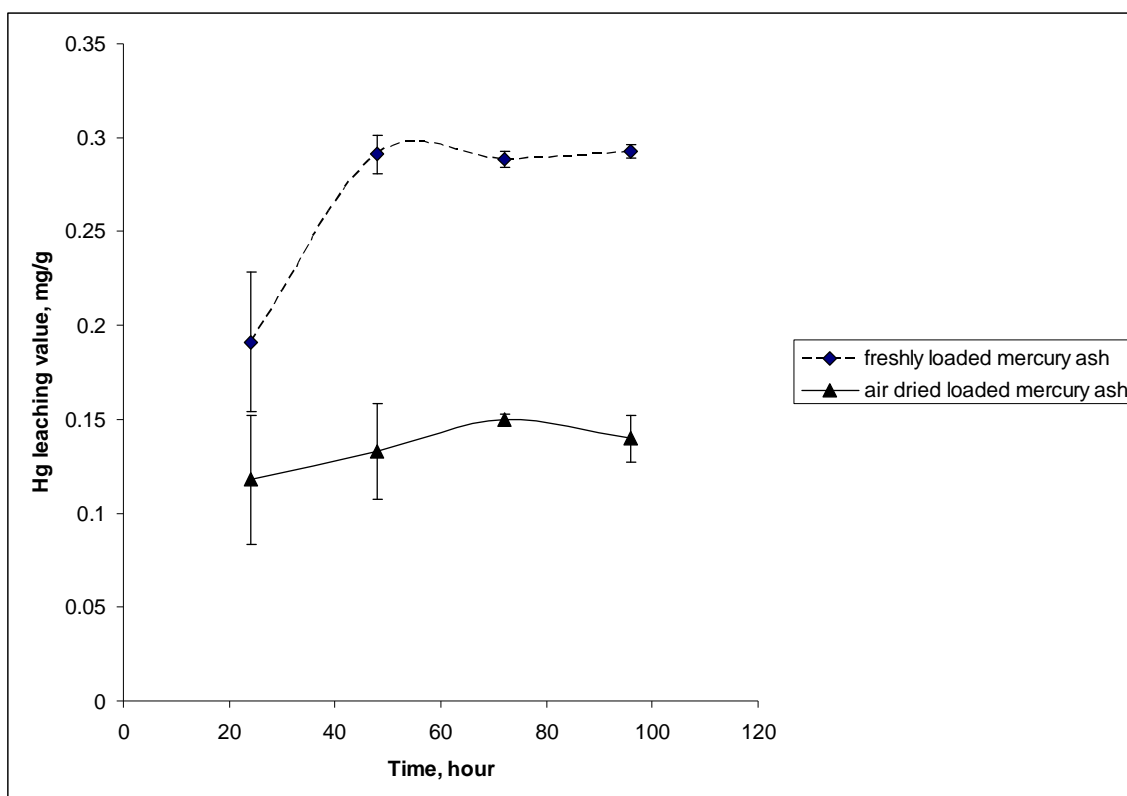
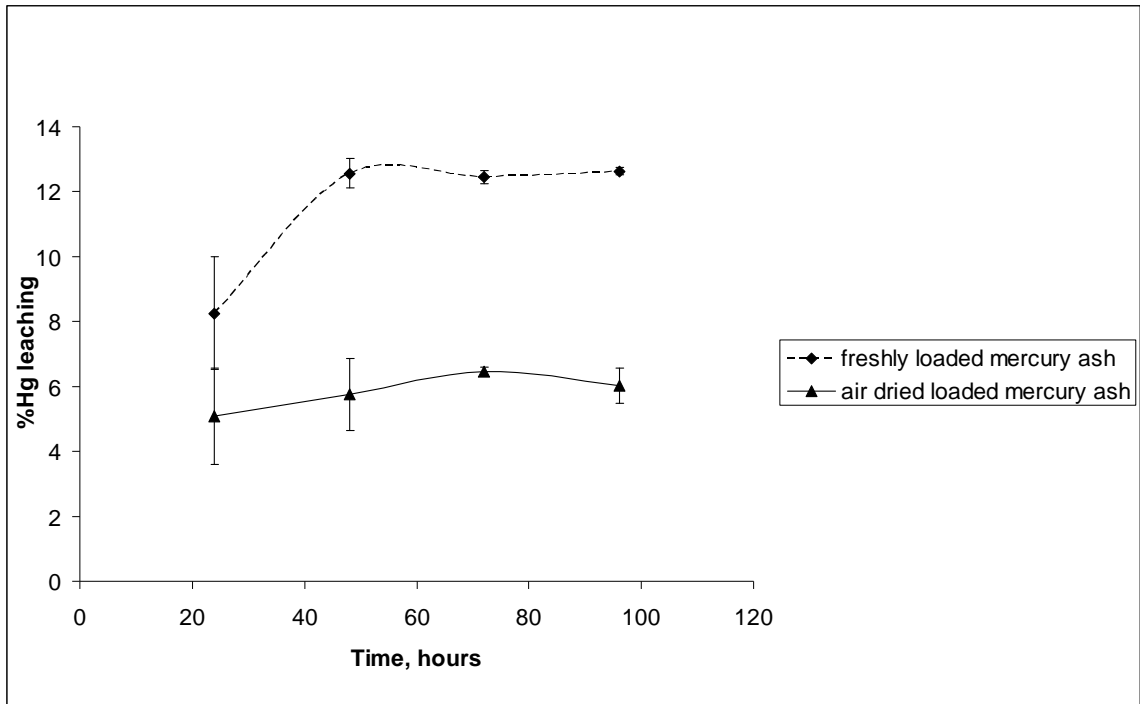


Figure 4-7 Time to equilibrium for leaching mercury from both wet and air dried samples of fly ash containing  $3 \text{ mg Hg g}^{-1}$  at pH 7.0

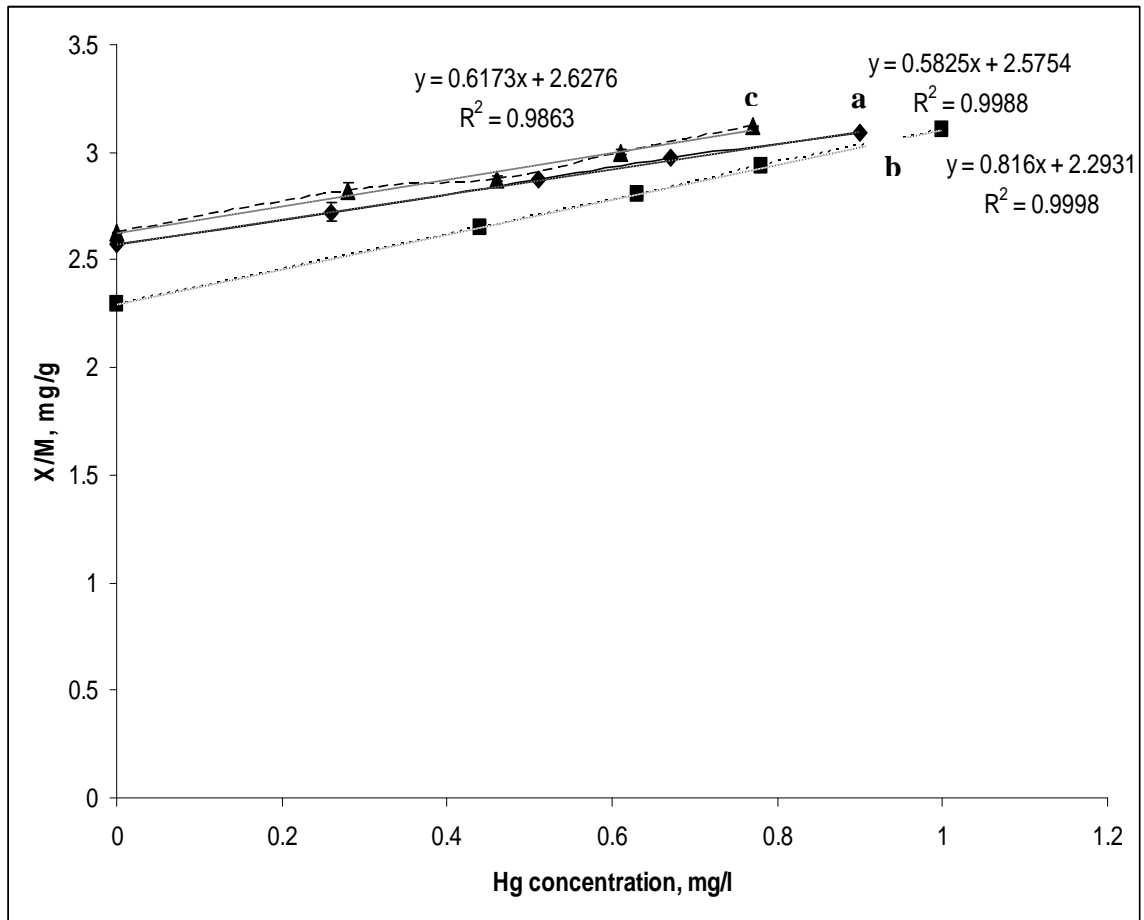


**Figure 4-8 Time to equilibrium for percentage of mercury leaching from both wet and air dried samples of fly ash containing  $3 \text{ mg Hg g}^{-1}$  at pH 7.0**

#### 4.4.2 Effect of pH on Hg loaded fly ash desorption

Figure 4-9 shows that most of the adsorbed mercury is not readily desorbed and that pH between 6 to 8 is not a major factor affecting its effectiveness in binding Hg from the environment.

The slope of the desorption coefficients for pH 6 ( $= 0.816$ ), for pH 7 ( $= 0.5825$ ), and for pH 8 ( $= 0.6173$ ) are not significantly different from one another, but the lines are extended backward. The amount of the  $3 \text{ mg g}^{-1}$  of Hg remaining on the ash at the end of desorption is  $2.29$ ,  $2.58$  and  $2.63 \text{ mg g}^{-1}$  at pH 6, 7 and 8, respectively. In other words, 72%, 81% and 83% of the mercury is not leachable at this pH range.



**Figure 4-9 Desorption isotherm of Hg loaded fly ash in 100 ml of DI water at pH 6, 7 and 8**

a) —◆— pH 7, b) --■-- pH 6, and c) -▲- pH 8

#### 4.5 Discussion

This study confirms that raw fly ash from the 4,000 Mwatt Ekibastuz Power Plant in Kazakhstan fired with high ash medium volatile coal can be used as a low cost adsorbent material at the natural pH of solution range (6 to 8). The results show that fly ash can immobilise low concentration of mercury due to its chemical properties and high unburnt carbon contained in the fly ash. The maximum adsorption capacity at equilibrium was 3.0  $\text{mg}\cdot\text{g}^{-1}$  which was close to that observed by Rio and Delebarre, (2003) in France's fly ash sample (3.2  $\text{mg}\cdot\text{g}^{-1}$  for silico-aluminous and 4.9  $\text{mg}\cdot\text{g}^{-1}$  for sulfo-calcic). This is most likely because the fly ash contained high concentration of unburnt carbon. The fly ash used in this study had more than ten times the unburnt carbon compared with fly ash used by Rio

and Delebarre, (2003). In their study of the removal of mercury by fly ash in aqueous solution in fluidized bed fly ash removal plants. They concluded that chemisorption (chemical bond) was the most likely form of uptake. In general, physisorption (physical bond) is the dominant phenomenon in adsorption mechanisms of activated carbon. The determination of carbon content containing in Ekibatuz fly ash was measured by three different methods (approximately 18% by using Elemental analyzer Flash EA1112 Series (see Appendix A), approximately 19% by using LOI determination method at 850°C (see Appendix A), and approximately 20% by using LOI determination method at 900°C (determined by Department of Science Service, Thailand). The results confirmed that the percentage of unburnt carbon containing in the fly ash was very high and close to 20%. Kazak Institute of Climate and Environment Monitor (1996) reported that Ekibastuz coal had carbon content of approximately 42%. According to the above only 50% of the carbon appear to have been burnt indicating that the combustion efficiency of Ekibastuz power plant was very low. The unburnt carbon content in Ekibastuz ash was twenty times higher than in Rio and Delebarre, (2003) samples from France which contained less than 1% unburnt carbon. Therefore, unburnt carbon could be the main factor affecting mercury adsorption of Ekibastuz ash at pH ranging from 6 to 8, and physical adsorption could be the major mechanism of adsorption as described by Crittenden et al. (2005). In principle, physical adsorption is not specific for which compounds sorbs to surface sites and has weaker forces and energies of bonding, and is more reversible than chemisorption (Crittenden et al., 2005). The comparison of mercury concentration which desorbed from wet and air dried ash showed that wet ash released more mercury than air dried ash. This may be because the structure of the ash surface changed during drying reducing the area for adsorption. Rio and Delebarre, (2003) showed using X-ray photoelectrons spectroscopy that adsorption mechanism of mercury in the French ash related to the oxide of calcium and aluminum and were formed in the hydration process. This may well explain the low exchange ability of part of the adsorbed mercury.

The pH of solution is the most important factor affecting the adsorption/desorption processes, due to the effect of pH on metal ion complex and metal ion mobility (James and Healy, 1972; Benjamin and Leckie, 1981; Elliot and Denny, 1982; Panday et al., 1985; Apak et al., 1998; Manceau et al., 2000; Hequet et al., 2001; Rao et al., 2002; Rio and



Delebarre, 2003; and Cho et al., 2005). Their studies found that low pH (acid condition) had higher metal ion mobility than high pH (over pH 7); therefore, there was more metal ion desorbed from spent adsorbent to solution when pH of solution was below 7. Rio and Delebarre (2003) study, for example, found that the leaching of air dried spent silico-aluminous and sulfo-calcic at pH 5 was 16.3% and 7.2% while desorption of mercury from air dried spent Ekibastuz ash at pH 7 was 6%. However, the results in this study (Figure 4-9) showed that pH of solution ranging from 6.0 to 8.0 normally found in the natural aquatic system had no significant effect on wet spent Ekibastuz ash mercury desorption and the concentration of mercury in leachate was accepted limit.

The further experiment was designed to study fly ash behaviours in aquatic system under anaerobic condition and organic rich with contaminated mercury.

## **Chapter 5**

### **Mercury Adsorption of Coal Fired Fly Ash**

#### **under Anaerobic Condition**

##### **5.1 Introduction**

The work described in this chapter was designed to test if fly ash could reduce the availability of Hg in water above organic rich fresh water sediments under reducing conditions.

##### **5.2 Determination of the ability of power station fly ash to immobilise Mercury in anaerobic rich organic sediments.**

Table 5-1 shows the results from the experiment to establish how effective fly ash is at stabilising mercury in anaerobic mercury rich sediments. It is important to note that when mercury was first added to the anaerobic organic rich sediments at a concentration of  $20 \text{ mg.l}^{-1}$ , the sediment effectively removed all available Hg in the aquatic phase. However, after 56 days mercury had been released into the water phase giving a concentration of  $52 \text{ }\mu\text{g.l}^{-1}$ . This is compatible with the literature which indicates that organic rich sediments release Hg into solution over time due to microbial activity (Ullrich, 2007).

After 56 days reaction time the effectiveness of fly ash at stabilising mercury in these anaerobic sediments is clear. The results not only show that fly ash is very effective in initially adsorbing Hg from solution, reducing concentrations to less than  $2 \text{ }\mu\text{g.l}^{-1}$ , but that it is also able to greatly reduce its solubility in water above the anaerobic organic rich sediments. In control A, which contained sediment alone there was no measurable mercury in solution, indicating the unpolluted nature of the rural forest catchment. Within the range of ash concentrations added the adsorption response was linear with the concentration being reduced to  $1.4 \text{ }\mu\text{g.l}^{-1}$  when 6 g of ash was added.

**Table 5-1 Effect of fly ash at stabilising Hg in anaerobic sediments**

Treatments	Hg concentration, $\mu\text{g.l}^{-1}$ (start)	Hg concentration, $\mu\text{g.l}^{-1}$ (8 weeks)
Silt	Less than 1 $\text{ng.l}^{-1}$	Less than 1 $\text{ng.l}^{-1}$
Silt + 20 $\text{mg.Hg l}^{-1}$	Less than 1 $\text{ng.l}^{-1}$	$51.6 \pm 3.4$
Silt + 20 $\text{mg.Hg l}^{-1}$ + 1.0 g fly ash	Less than 1 $\text{ng.l}^{-1}$	$7.3 \pm 1.0$
Silt + 20 $\text{mg.Hg l}^{-1}$ + 6 g fly ash	Less than 1 $\text{ng.l}^{-1}$	$1.4 \pm 0.2$

Figure 5-1 shows the equilibrium of Hg in sediments and solution after 56 days and compares it with the equilibrium concentration between mercury in solution and fly ash in the absence of sediment. (See Chapter 4) The concentration of Hg added in the initial solution of the anaerobic treatment was 20  $\text{mg.l}^{-1}$ , but the final concentration in solution above organic rich sediments containing no Hg fell to 52  $\mu\text{g.l}^{-1}$ . Under anaerobic with organic rich sediment condition, it appears that fly ash does not form an equilibrium with the Hg adsorbed on the sediment. On the other hand, under aerobic condition containing no sediment the adsorption equilibrium occurs as shown in a water/ash experiment.

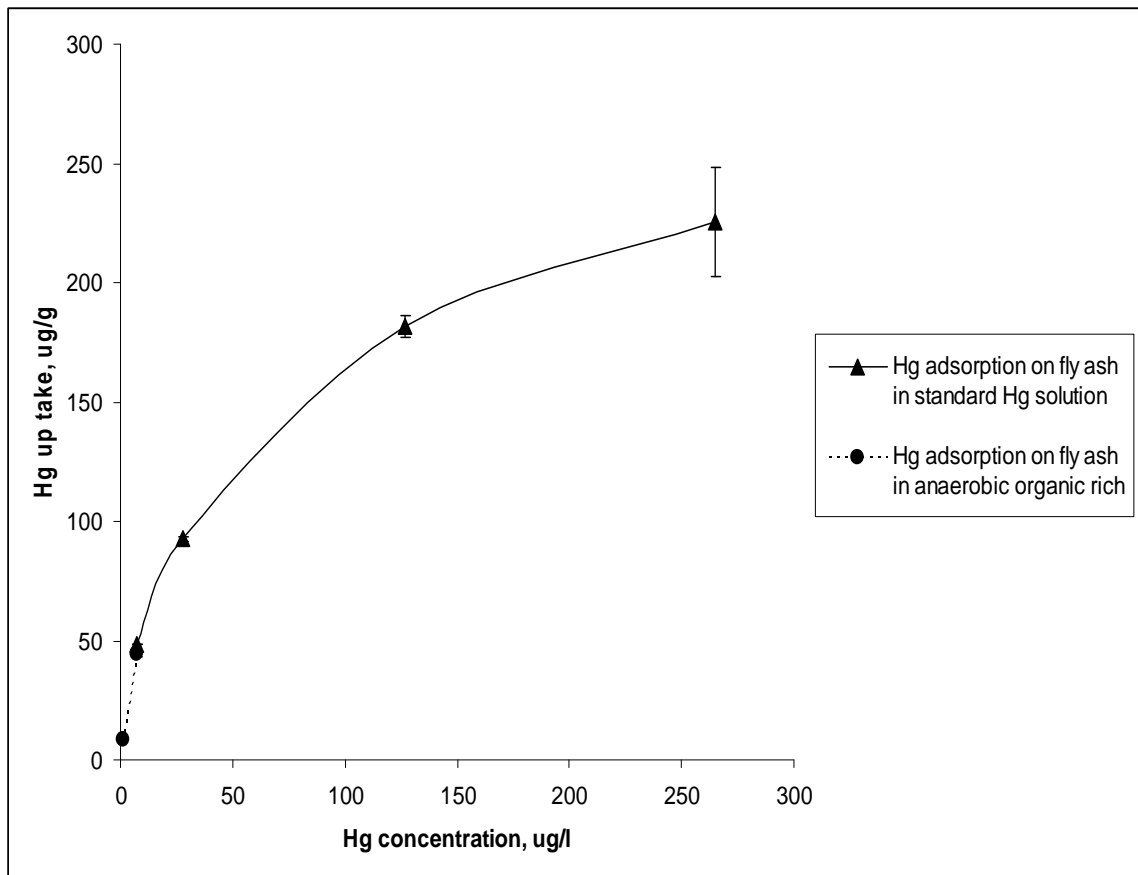




Figure 5-1 Comparison of equilibrium between mercury concentration in aerobic solution and fly ash,  and mercury in anaerobic solution containing organic rich sediments, at pH 7.0 

### 5.3 Determination of the importance of unburnt carbon in fly ash and its ability to immobilise Mercury in anaerobic rich organic sediments.

Table 5-2 compares the equilibrium of Hg in water in anaerobic organic rich environments and 2 samples of fly ash, a raw sample of ash and one that has been heated to remove unburnt carbon. Approximately 24% and 56% of Hg was adsorbed from the solution by 0.1 g and 0.6 g per 100 ml mixture of the thermal treated fly ash (carbon removed), compared with 86% and 97% by the raw fly ash (see Table 5.1). It is clear that if the current amount of Hg polluted added to anaerobic organic rich sediments, it is able to reduced the concentration in solution to below the accepted limit ( $1.4 \mu\text{g.l}^{-1}$  for surface water) (USEPA,2008). There is, however, still low mercury concentration in the solution.

**Table 5-2 Effect of fly ash at stabilising Hg in anaerobic sediments (Carbon burnt)**

Treatments	Hg concentration, $\mu\text{g.l}^{-1}$ (start)	Hg concentration, $\mu\text{g.l}^{-1}$ (8 weeks)
Silt	Less than 1 $\text{ng.l}^{-1}$	Less than 1 $\text{ng.l}^{-1}$
Silt + 20 $\text{mg.Hg l}^{-1}$	Less than 1 $\text{ng.l}^{-1}$	$51.6 \pm 3.4$
Silt + 20 $\text{mg.Hg l}^{-1}$ + 1.0 g carbon burnt fly ash	Less than 1 $\text{ng.l}^{-1}$	$39.2 \pm 1.9$
Silt + 20 $\text{mg.Hg l}^{-1}$ + 6.0 g carbon burnt fly ash	Less than 1 $\text{ng.l}^{-1}$	$22.4 \pm 1.0$

Figure 5-2 compares the equilibrium between mercury in anaerobic solution containing organic rich sediment with a) raw fly ash and b) fly ash that has been burnt to remove unburnt carbon. The graph confirms that the unburnt carbon content contained in raw fly ash is a very important compound for mercury adsorption. The adsorption equilibrium of the carbon free ash is much less favourable for stabilising Hg in anaerobic aquatic media. It is clear that carbon content of a particular fly ash is the key to its effectiveness in stabilising mercury in aquatic condition, although carbon free ash is able to adsorb Hg best to a less extent.

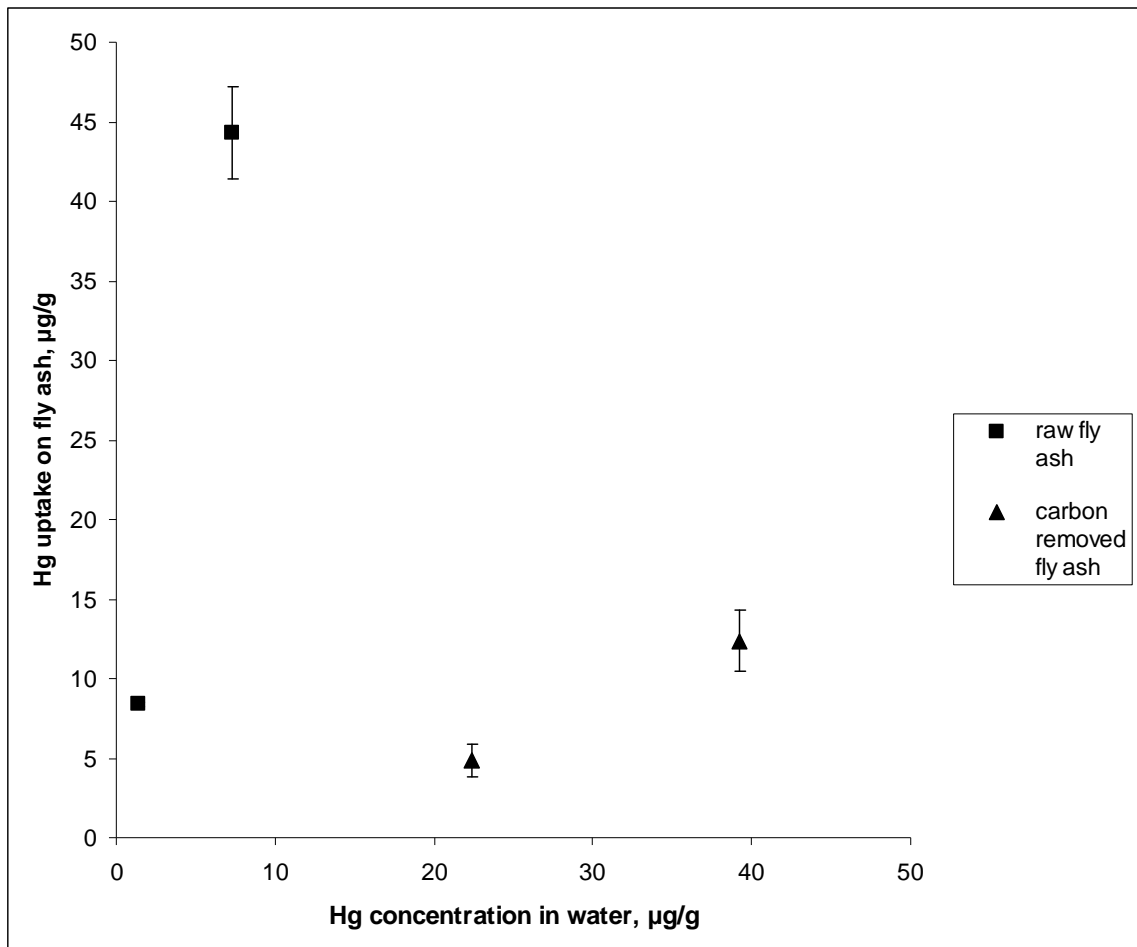


Figure 5-2 Uptake equilibrium of Hg after 56 days between mercury adsorbed onto fly ash within an anaerobic solution containing organic rich sediments,

■ ) raw fly ash,      ▲ ) carbon removed

#### 5.4 Effects of fly ash on pH of anaerobic solutions

Adding raw fly ash caused the pH of the solutions to initially slightly rise, but adding burnt ash produced no increase in initial pH. Over the 56 days experimental period the pH of the solutions raised significantly, the rise being greater in the samples when fly ash had been added. The delay in the rise in pH is likely to be the result of the low solubility of the calcium oxide in the fly ash (see chemical composition of Ekibatuz fly ash from Table 3-1)

**Table 5-3 The Results of pH of Solution at Day 0 and Day 56**

Treatments	Day0	Day 56
	pH	pH
Silt	6.2	7.0
Silt + 20 mg.Hg	6.5	6.8
Silt + 20 mg.Hg + 1 g raw fly ash	6.7	7.9
Silt + 20 mg.Hg + 6 g raw fly ash	6.9	8.3
Silt + 20 mg.Hg + 1 g carbon burned fly ash	6.5	7.8
Silt + 20 mg.Hg + 6 g carbon free fly ash	6.5	8.2

### 5.5 Discussion

The results show that adding fly ash to anaerobic sediments significantly reduced the amount of Hg being released into the water column. This is in keeping with the results in Chapter 4 and Table 5-1. The ability of fly ash to adsorb mercury from water is greatly dependent on the presence of unburnt carbon; however, in the absence of carbon the ash can still reduce the amount of Hg in solution (See Table 5-2) suggesting that the ash itself plays an important role in reducing mercury solubility (See chemical composition of Ekibatuz fly ash from Table 3-1). Throwarth et al. 2005 suggested that high contents of calcium oxide (CaO), magnesium oxide (MgO), silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>) and ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) in fly ash can increase the adsorption of Hg on fly ash. This study indicated that the chemical compositions which contained in fly ash can be bonded with mercury by chemical bond.

The amount of mercury that the ash can adsorb is only 3.0 kilograms per ton. The question then arises whether its stabilising capacity is adequate to stabilise the low concentration of mercury pollution in the natural environment. The answer to this question is likely to be that in many cases it would be. For example, in the heavily polluted Lake Balkyldak, a 15 km<sup>2</sup> waste water lagoon of the disused Pavlodar Plant mercury concentrations in the bed

sediments ranged from 0.11 to 1,500 mg kg<sup>-1</sup> with a typical bed load of 10 to 15 ton (Ullrich, 2007). To provide full stabilisation this would require between 3.3 and 5.0 kg of ash to be added per m<sup>2</sup> of bed.

Most solubilisation of mercury takes place in the aquatic environment through anaerobic biological methylation to form the highly toxic soluble methylmercury. The results from the experiment to confirm its effectiveness in stabilising mercury in anaerobic sediments showed that Ekibastuz fly ash was highly effective in stabilising mercury in anaerobic condition with organic rich sediments, preventing the concentration of soluble mercury in solution to rise above the water quality standard of mercury in surface water recommended by The Federal Clean Air Act and USEPA (2008) (1.4 µg.l<sup>-1</sup>), even though water quality standard of mercury in drinking water recommended by the WHO (2005) was 1 µg.l<sup>-1</sup>.

It can therefore be concluded that fly ash from Ekibastuz appears to be effective in limiting the environmental availability of mercury in the aquatic environment. This is confirmed by observations in the River Nura in Central Kazakhstan that despite very high concentrations of mercury in bed sediments, there were low concentrations of mercury in filtered water samples and only slightly elevated mercury in fish (Ullrich, 2007). The authors explained this by the fact that most of the mercury ion in the sediments was adsorbed on approximately 6 million tons of fly ash.

According to the experiment (see Chapter 3 section 3.2.7.2), adding fly ash to the reactors caused the pH to rise from 6.5-6.7 to 7.8-8.3 (Table 5-3). Many researches studying methylation in lakes showed that low pH favoured solubilisation of Hg (Xun and Campbell, 1987; Miskimmin, 1991; Craig and Moreton, 1983; and Winfrey and Rudd, 1990). Both Xun and Miskimmin found that methyl mercury concentrations increased at low pH lake water due to the reduced binding of inorganic mercury to dissolved organic carbon, then therefore increased the Hg (II) availability for methylation. The low concentration of methyl mercury found at high pH lakes because the formation of volatile dimethylmercury and the volatilization of Hg<sup>0</sup> (Craig and Moreton, 1983; Winfrey and Rudd, 1990).

The question then arises as to whether unburnt carbon on pH is the main factor that results in fly ash being very effective at reducing soluble mercury.



This issue is resolved by looking at the results in Table 5-1, 5-2 and 5-3 which showed that the concentration of dissolved Hg fell by  $1.4 \mu\text{g.l}^{-1}$  (97.3%) when  $6 \text{ g l}^{-1}$  raw fly ash was added, but only fell by  $22.4 \mu\text{g.l}^{-1}$  (55.6%) when burnt ash (carbon free) was added. There was no significant difference in the pH; however, both treatments indicated that unburnt carbon was the main factor limiting the solubility of Hg.

## **5.6 Conclusion**

Fly ash is effective in reducing the solubility of mercury in anaerobic condition with organic rich sediments and the main part of fly ash that determines its effectiveness is the unburnt carbon content. In other words, the ability of a particular ash in reducing the solubility of Hg depends on the amount of unburnt carbon in the ash.

## Chapter 6

### Conclusion

This study was to establish if fly ash from the 4,000 Mwatt Ekibatuz Power Plant in Kazakhstan to stabilise low concentrations of soluble mercury in the environment. The most toxic form of mercury is organic mercury. In the Aquatic environment methyl mercury is particularly problematic as it accumulates in the aquatic food chain and finally ends up at high concentrations in predatory fish. Since fish pose the major pathway for human intake it is important to disrupt the pathway of intake, (Ullrich et al., 2001). The logical place to break this pathway is to prevent methylation taking place in the aerobic sediments.

The results in Chapters 4 and 5 showed that fly ash from Ekibatuz Power Plant is able to rapidly adsorb mercury from aquatic solution up to an adsorbed concentration of  $3.0 \text{ mg.g}^{-1}$ , and that once adsorbed it is fairly tightly bound with little desorption taking place over the range of pHs likely to be found in aquatic ecosystems. Although maximum adsorption was observed at pH 7.0 the amount of mercury adsorbed remained fairly consistent between pHs 6.0 and 8.0, and hence the above results suggest that the ash provides a reliable method of stabilising low concentrations of mercury in the sediments of the aquatic environment. Mercury concentration released from both wet and air dried ash were at acceptably low concentration.

The research showed that although some of the mercury was bound to the inorganic fraction of the ash, some 40% of it was bound onto the unburnt carbon in the ash (Table 5-1, Table 5-2 and Figure 5-2). Ekibastuz fly ash is very high in unburnt carbon (see Table 3-1). Rio and Delebar (2003) found 1% of unburnt carbon, while Ekibastuz fly ash used in this study showed that the unburnt carbon fraction was 18%. This is very high compared with most fly ash produced by more modern power plants, typically between 0.1 and 7.0 wt% (Waller and Brown, 1996). It is therefore too premature to make state that fly ash is a

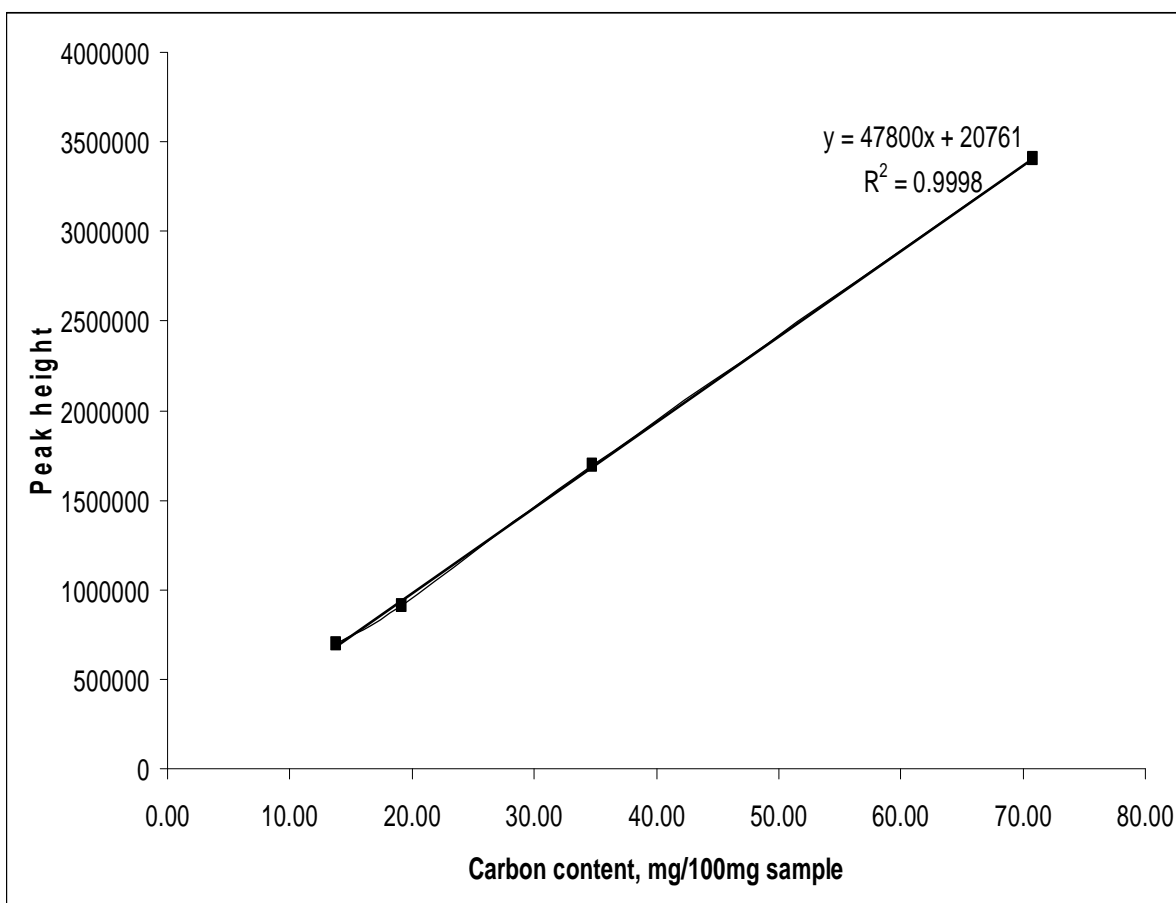
suitable and economical option for stabilising low concentrations of mercury in the aquatic environment.

Further work is needed on the wider use of fly ash as low cost adsorbent material for remediation of mercury problems such as mercury capture from emission gas, mercury removal from wastewater and immobilisation of mercury in soil. Indeed it may be possible to predict the likely effectiveness of an ash in a particular polluted environment by establishing its unburnt carbon content.

The second note of caution comes from the fact that although fly ash is likely to be effective for stabilising mercury, there is the practical problem of keeping contaminated fly ash in place until it has captured the available mercury. This problem is likely to be particularly acute in rivers at a time of flood and in shallow lakes where waves and current actions are expected to redistribute contaminated fly ash over time and could remove from the contaminated area. The monitoring programme of mercury concentrations at contaminated area is also necessary to set up.

### Appendix A : Unburnt Carbon content determination by using Elemental Analyzer Flash EA1112 Series

Sample ID	Sample weight (mg)	Peak height	
Reagent Blank (1)		11271	
Reagent Blank (2)		10011	
Reagent Blank (3)		8086	
Reagent Blank (4)		8151	
	Average blank	9379.75	
Sample ID	Sample weight, (mg)	Peak height	%Carbon content
Ekibatuz fly ash-1	9	7618092	17.63819444
Ekibatuz fly ash-2	6.4	5293576	17.42422094
Ekibatuz fly ash-3	5.4	4766103	18.57730339
		Average	17.88
Calibration curve			
Sample ID	Carbon content, mg/100mg sample	Peak height	
Reference standard 1	13.79	693855.25	
Reference standard 2	19.18	913933.25	
Reference standard 3	34.78	1694659.25	
Reference standard 4	70.84	3404911.25	



Appendix A : Unburnt Carbon content determination by  
loss-on-ignition

Sample No.	Sample weigh, g		Weigh loss, g	L.O.I
	Before	After		
1	4.303	3.432	0.871	20.24
2	4.298	3.480	0.818	19.03
3	3.883	3.099	0.784	20.19
4	4.064	3.277	0.787	19.37
5	3.788	3.082	0.706	18.64
6	4.340	3.491	0.849	19.56
7	4.055	3.331	0.724	17.85
8	4.160	3.374	0.786	18.89
			<b>Average of LOI</b>	<b>19.22</b>

## Appendix B

### Student's t-test of Mercury adsorbed onto PET bottle Result

**TableB-1 The result of mercury adsorbed onto 500 ml of Coke bottle**

	Hg concentration, mg.l <sup>-1</sup> (Before shaken)			Hg concentration, mg.l <sup>-1</sup> (After shaken)		
	0	0.1	50	0	0.1	50
Replicate 1	-0.182	0.096	55.28	-0.167	0.096	54.42
Replicate 2	-0.162	0.095	55.32	-0.168	0.095	54.35
Replicate 3	-0.145	0.099	57.59	-0.143	0.102	57.85
Replicate 4	-0.144	0.101	57.73	-0.144	0.101	56.10

**TableB-2 Student's t-test calculation**

Mercury concentration, mg l <sup>-1</sup>	Paired Differences					t	df	p-value
				95% Confidence Interval of the Difference				
	Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1 ZeroPre - ZeroPost	-.00275	.00885	.00442	-.01683	.01133	-0.662	3	0.578
Pair 2 0.1Pre – 0.1Post	-.00075	.00150	.00075	-.00314	.00164	-1.000	3	0.391
Pair 3 50Pre - 50Post	.80000	.78422	.39211	-.44787	2.04787	2.040	3	0.134

At Hg concentration 0, 0.100, and 50.00 mg.l<sup>-1</sup>, the p-value was over 0.05 therefore no significant different of mercury concentrations between before and after shaken mercury solution into 500 ml of Coke bottles at 95% confidence levels.

## Appendix C

### Calculation of $C_e$ and X/M follows Freundlich Equation

**Table C-1** Adsorption equilibrium in initial solution pH 6.0 and initial Hg concentration  $500 \mu\text{g.l}^{-1}$

Sample No.	Fly ash dosage, g	Volume, L	Residual Hg, ( $C_e, \text{mg.l}^{-1}$ )	Adsorpted/adsorbent ( $X/M, \text{mg.g}^{-1}$ )
1	0.100	0.100	0.412	0.088
2	0.100	0.100	0.441	0.059
3	0.100	0.100	0.390	0.110
4	0.200	0.100	0.333	0.084
5	0.200	0.100	0.372	0.064
6	0.200	0.100	0.279	0.111
7	0.500	0.100	0.146	0.071
8	0.500	0.100	0.124	0.075
9	0.500	0.100	0.165	0.067
10	1.00	0.100	0.029	0.047
11	1.00	0.100	0.030	0.047
12	1.00	0.100	0.033	0.047



**Table C-2** Adsorption equilibrium in initial solution pH 7.0 and initial Hg concentration  $500 \mu\text{g.l}^{-1}$

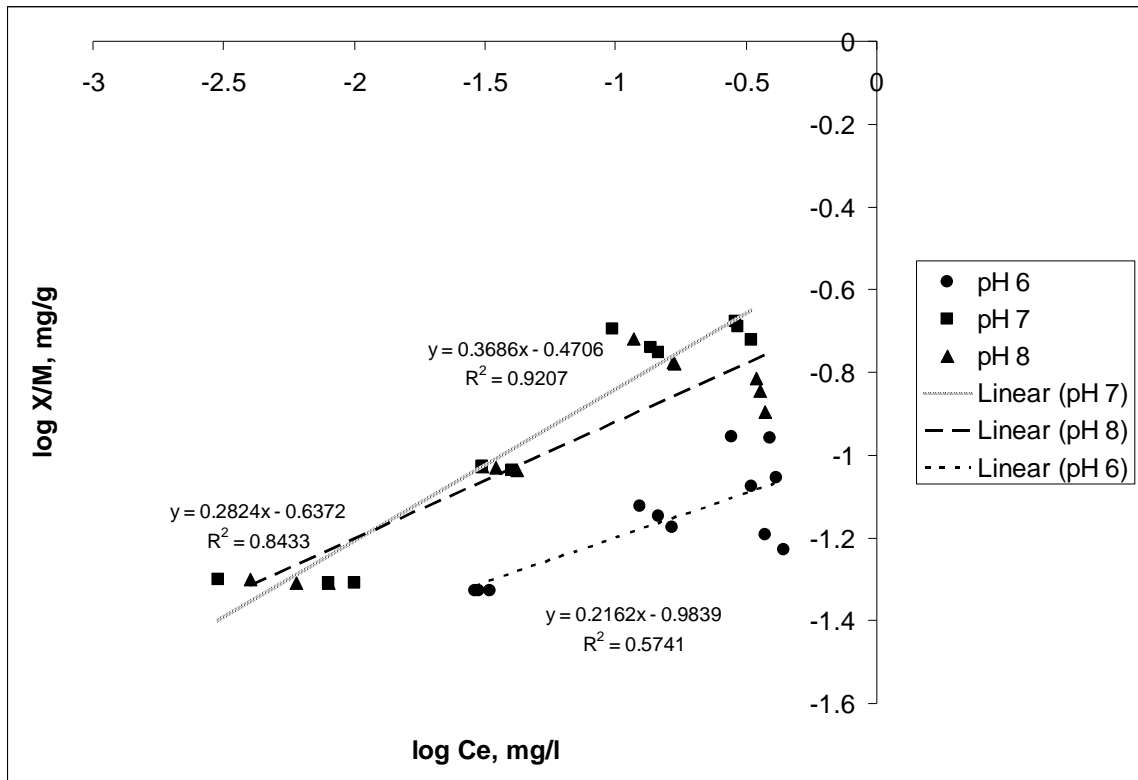
Sample No.	Fly ash dosage, g	Volume, L	Residual Hg, (Ce, $\text{mg.l}^{-1}$ )	Adsorpted/adsorbent (X/M, $\text{mg.g}^{-1}$ )
1	0.100	0.100	0.311	0.189
2	0.100	0.100	0.289	0.211
3	0.100	0.100	0.295	0.205
4	0.200	0.100	0.146	0.177
5	0.200	0.100	0.137	0.182
6	0.200	0.100	0.097	0.202
7	0.500	0.100	0.031	0.094
8	0.500	0.100	0.040	0.092
9	0.500	0.100	0.031	0.094
10	1.00	0.100	0.010	0.049
11	1.00	0.100	0.008	0.049
12	1.00	0.100	0.003	0.050

**Table C-3** Adsorption equilibrium in initial solution pH 8.0 and initial Hg concentration  $500 \mu\text{g.l}^{-1}$

Sample No.	Fly ash dosage, g	Volume, L	Residual Hg, (Ce, $\text{mg.l}^{-1}$ )	Adsorbed/adsorbent (X/M, $\text{mg.g}^{-1}$ )
1	0.100	0.100	0.357	0.143
2	0.100	0.100	0.347	0.153
3	0.100	0.100	0.373	0.127
4	0.200	0.100	0.118	0.191
5	0.200	0.100	0.166	0.167
6	0.200	0.100	0.169	0.166
7	0.500	0.100	0.031	0.094
8	0.500	0.100	0.035	0.093
9	0.500	0.100	0.042	0.092
10	1.00	0.100	0.008	0.049
11	1.00	0.100	0.006	0.049
12	1.00	0.100	0.004	0.050

**Table C-4** Log  $C_e$  and log  $X/M$  of adsorption equilibrium pH 6, 7 and 8  
initial Hg concentration  $500 \mu\text{g.l}^{-1}$

pH_6		pH_7		pH_8	
log $C_e$	log $X/M$	log $C_e$	log $X/M$	log $C_e$	log $X/M$
-0.38510	-1.05552	-0.48017	-0.72354	-0.44733	-0.84466
-0.35556	-1.22915	-0.53910	-0.67572	-0.45967	-0.81531
-0.40894	-0.95861	-0.53018	-0.68825	-0.42829	-0.89620
-0.47756	-1.07572	-0.83565	-0.75203	-0.92812	-0.71897
-0.42946	-1.19382	-0.86328	-0.73993	-0.77989	-0.77728
-0.55440	-0.95468	-1.01323	-0.69465	-0.77211	-0.77989
-0.83565	-1.14874	-1.50864	-1.02687	-1.50864	-1.02687
-0.90658	-1.12494	-1.39794	-1.03621	-1.45593	-1.03517
-0.78252	-1.17393	-1.50864	-1.02687	-1.37675	-1.03621
-1.53760	-1.32790	-2.00000	-1.30980	-2.09691	-1.30980
-1.52288	-1.32790	-2.09691	-1.30980	-2.22185	-1.30980
-1.48149	-1.32790	-2.52288	-1.30103	-2.39794	-1.30103



**Freundlich isotherm;**

$$\frac{X}{M} = K_f C_e^{1/n}$$

$$\log \frac{X}{M} = \log k_f + \frac{1}{n} \log C_e$$

**Example of calculation**

A graph of  $\log X/M$  versus  $\log C_e$  was plotted and found to follow a linear path as shown above.

From the graph at pH 6 given the equation:

$$y = 0.2162x - 0.9839$$

Intercept =  $\log k = (-0.9839)$

On taking log out =  $k = 0.104$

Slope  $dy/dx = 0.2162 = (1/n) \log C_e$

On taking log out =  $1/n = 1.6451$

On taking inverse  $1.6451^{-1} = 0.608$

From the graph at pH 7 given the equation:

$$y = 0.3686x - 0.4706$$

Intercept =  $\log k = (-0.4706)$

On taking log out =  $k = 0.338$

Slope  $dy/dx = 0.3686 = (1/n) \log C_e$

On taking log out =  $1/n = 2.3367$

On taking inverse  $2.3367^{-1} = 0.428$

From the graph at pH 8 given the equation:

$$y = 0.2824x - 0.6372$$

Intercept =  $\log k = (-0.6372)$

On taking log out =  $k = 0.231$

Slope  $dy/dx = 0.2824 = (1/n) \log C_e$

On taking log out =  $1/n = 1.916$

On taking inverse  $1.916^{-1} = 0.522$

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