

KINETIC STUDY ON THE REMOVAL OF MERCURY BY FLY ASH

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Received: 17/09/2013

Accepted: 17/02/2014

Available online: 19/02/2014

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ABSTRACT

The removal of mercury by adsorption process using fly ash was investigated in this study. Mercury removal capacity of fly ash was performed by batch mode adsorption experiment with the effect of various parameters i.e., contact time (0.5-3.5) h, pH of 2-10, concentration of adsorbate (1, 5 and 10) mg l⁻¹, adsorbent dose (100-1000) mg per 100 ml solution and temperature (303, 313 and 323) K. Mercury concentration (10 mg l⁻¹) was chosen for all parameters except adsorbent dose. The experimental data were showed that the adsorbent dose of 200, 400 and 600 mg per 100 ml were sufficient to maximum removal of mercury (98 percent) from aqueous solution of mercury (1, 5 and 10) mg.L⁻¹ at equilibrium and 89 percent mercury was removed when concentration was 10 mg l⁻¹ at 303K temperature. Adsorbent dose of 100 mg per 100 ml solution showed 74 percent removal of mercury for 2 hours contact time and 90 percent removal at pH 10. The experimental data were fitted with pseudo first order and pseudo second order kinetics which was proposed by Lagergreen. The value of pseudo first order rate constant, k_1 is 0.697 h⁻¹ and pseudo second order rate constant k_2 is 0.135 l mg⁻¹ h⁻¹.

Keywords: Adsorption, Fly ash, Contacts time, pH, Adsorbate concentration, Adsorbent dose and Temperature.

1. Introduction

Mercury is a well known toxic metal in nature, occurring widely in environment as heavy metal pollutants. Mercury found to be hazardous for the living organism in two ways, intake by water bodies as in liquid form and from water bodies to human bodies and another one is mercury vapors inhaled by living organism. It enters within cells through the blood stream in the lungs. Mercury and its derivatives are toxicant and insidious poisonous having mercury pollutant including environmental (Horvat M. *et al.*, 1964) and human being health impact (Horvat M., 1964) such as carcinogenic, mutagenic, teratogenic, intestinal and urinary complications.

Mercury and its inorganic compounds are mainly causes of disorders of the chromosomes, pulmonary functions, intestinal activities, urinary and kidneys function, etc are the major symptoms of mercury poisoning [Berglund F. and Berlin M., 1969]. The central nervous system is also affected when mercury concentration being exceeded over the tolerance limit, which is 1 ppm for drinking water and 10 ppm for ground water prescribed in India by Bureau of Indian Standard. Mercury and its derivatives are causes of many diseases and disorders i.e., neural, cardiovascular system, bones, kidneys, skin, brain, liver, Spleen, eyes and lungs (Clarkson, 1993; Sigel and Sigel, 1997). Toxicological effects of mercury are neurological damage, paralysis, blindness and birth defects. Milder symptoms include dispersion and irritability (Zang *et al.*, 2005; Grim J., 1998). These diseases made a major problem to the living being in

normal life and ultimately may causes of death. A well-known environmental incident of mercury toxicity was found in Minamata Bay, Japan during 1953-1960, where thousands of people suffered from mercury poisoning pollution through fish, called "Minamata disease" (Rangel-Mandez and Street, 2002).

In India, the main sources of mercury pollution is based on those industries which work/production is based on mercury cell process. Although industries have been converted environment friendly (membrane based process), how ever still 50% of chlor alkali industries are based on mercury cell process, and these are paper & pulp, paints, cement, fertilizer, pesticides, cinnabar, pharmaceuticals, battery and vinyl chloride manufacturer industries. Hence the removal of mercury from these hazardous wastes is most important task to control the mercury pollution and prevent the diseases caused by mercury in bio-organism & human beings.

Various important and innovative treatment technique have been used for the removal of mercury include, ion-exchange (Grau and Bisang, 1995; Beck *et al.*, 1995), co-agulation (Patterson, 1975), sulphide precipitation (Krishna *et al.*, 1993; Brook-Devlin, 1992), membrane & ultra filtration (Barron-Zambrano, 2002), adsorption (Grayson, 1981; Bakta *et al.*, 2010; Noah *et al.*, 2012), liquid-liquid extraction (Mitsui Jon, 1985; Baba Y. *et al.*, 1992) and other separation methods. Among these techniques adsorption process is widely used in the removal of mercury from liquid and aqueous phase by low-cost adsorbent. Activated carbon and ceramic clay are the typical adsorbent for removing mercury from aqueous phase (Bhakta and Munikage, 2009). However, most of the adsorbents are expensive. Therefore, beside of other activated carbon, fly ash is a cheap and best adsorbent give good and encouraging results for the removal of mercury from aqueous solution.

On account of above point of view, though various adsorption media have been developed for the removal of mercury, but many of them are costly and in some cases had adverse environmental impact. Therefore the present study has an attempt to investigate the effect of fly ash in various intrinsic and extrinsic factors (contact time, pH, adsorbate concentration, adsorbent dose and temperature) which have greatly influence in the heavy metal removal mechanism. The adsorption method is used for removal of mercury ions from mercuric chloride solution on to fly ash in the liquid phase takes places in this study.

2. Materials And Methods

2.1. Adsorbate

Different concentration of mercury (1, 5 and 10) mg l⁻¹ solution were prepared by using mercuric chloride which was purchased from Fisher Scientific, Mumbai, India, as a source of mercury.

2.2. Adsorbent

Fly ash is a cheap substitute of commercially available adsorbents having functional groups i.e., >CO and -COOH.

It was collected from Panki Thermal power Station, Panki, Kanpur, India. It is alkaline and abrasive in nature and chemically inert at low temperature, which is mainly composed of few oxides derived from inorganic compound which remain unburned after combustion. The scanning electron microscope (SEM) images and physicochemical characteristics of fly ash are given in figure 1 (a & b) and table 1 respectively. The fly ash images were obtained by using scanning electron microscope (model No.: ZEISS EVO 50).

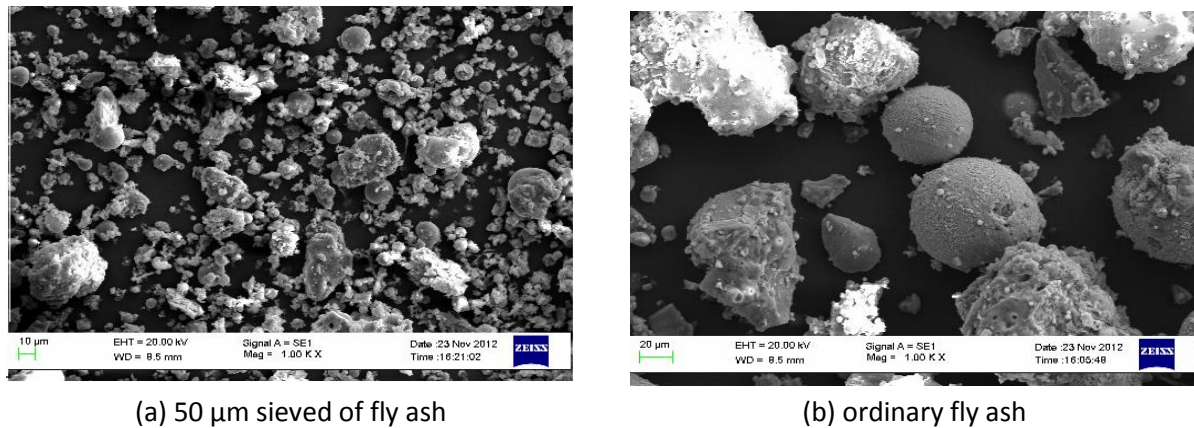


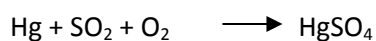
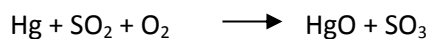
Figure 1. SEM images of fly ash

Table 1. Physicochemical characteristics of fly ash

Constituents	Percentage weight
SiO ₂	48.65
Al ₂ O ₃	19.90
Fe ₂ O ₃	6.26
CaO	3.7
MgO	1.51
K ₂ O	1.48
N ₂ O	0.11
SO ₃	0.06
TiO ₂	1.1
LOI (Loss of ignition)	0.5
Moisture content (%)	19
Retention on 50 µm sieve	2.34
Drying shrinkage, percentage	0.06
Soundness by autoclave expansion, percentage	0.05
Compressive strength	80

2.3. Experimental procedures

A stock solution of mercury was prepared by dissolving 0.2715 g of HgCl₂ in 100 ml distilled water in a 250 ml glass stoppered conical flask containing 0.1 ml of concentrated hydrochloric acid and diluting it up to 250 ml mark. Dilute this stock solution again to attain the desired concentration of mercury and used in order to study the effect of different parameters i.e., contact time (0.5-3.5) h, pH (2-10), adsorbate concentration (1, 5 and 10) mg l⁻¹, adsorbent dose (100-1000) mg per 100 ml solution and temperature (303, 313 and 323) K. To attain equilibrium and the residual concentration of mercury was subsequently determined under batch experiment. The Mercury was removed by fly ash containing oxide of sulphur in the form of HgO and HgSO₄



The concentration of mercury before and after treatment was analyzed using UV-VIS Spectrophotometer (model JASCO 7800). The mercury removal percentage (MRP) was calculated by the following equation:

$$\text{Removal percentage} = 100 \times \frac{(C_i - C_e)}{C_i} \quad (1)$$

Where, C_i and C_e are the initial and equilibrium (final) concentrations of mercury in mg l^{-1} respectively.

3. Results and discussion

3.1. Effect of contact time

The Figure 2 shows the effect of contact time for mercury removal percentage on to fly ash. The initial concentration of (10 mg l^{-1}) mercury was taken in the experiment and solution was treated with fixed dose of adsorbent $100 \text{ mg per } 100 \text{ ml}$ solution. The removal of mercury increased with time and attains equilibrium in 2 hours. At equilibrium 74 percent removal of mercury was achieved. It is evident from the figure 2, that the contact time of 2 hours was selected for all the subsequent experiments.

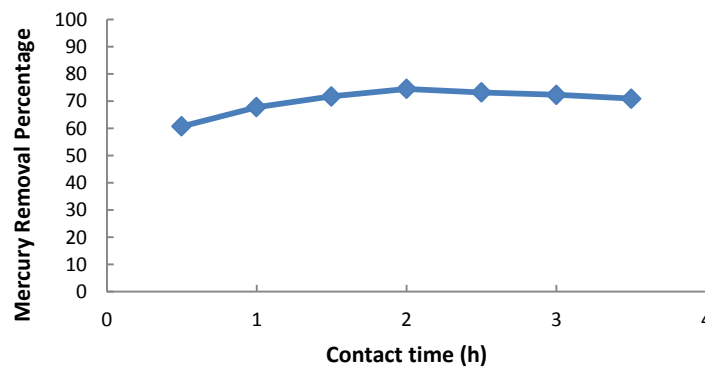


Figure 2. Effect of contact time on the removal of mercury

3.2. Effect of pH

The pH is a most important parameter to controlling the adsorption of mercury from waste water and aqueous solutions as it may affect the surface charge of adsorbent as well as the degree of ionization of different pollutants.

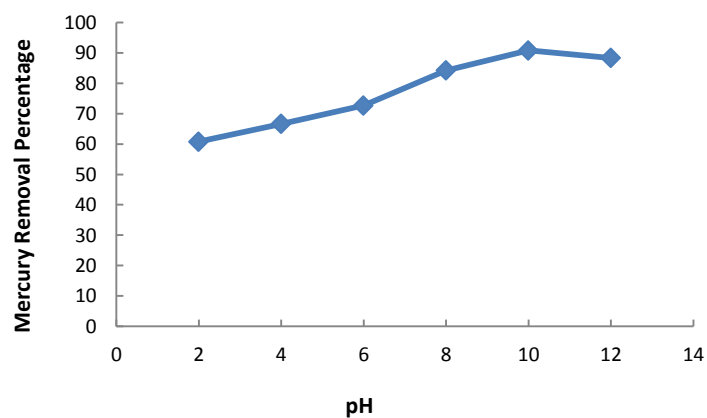


Figure 3. Effect of pH on the removal of mercury

Figure 3 shows the effect of pH on the removal of mercury on to fly ash. The experiment conducted at fixed temperature (303 K) and contact time duration 2 hours with the variation of pH from acidic range to basic range. The effect of initial pH for the adsorption of mercury by fly ash was studied to find out appropriate pH for the maximum efficiency of the process. It is showed from the experimental results that the removal of mercury was increased from 60 to 90 percent at pH 2-10 and then decrease. The maximum adsorption was found to be 90 percent at pH 10.

3.3. Effect of adsorbate concentration and adsorbent dose

For investigation of effect of adsorbate, mercury concentration of (1, 5 and 10 mg l⁻¹) were taken and treated with different doses of adsorbent (100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000) mg per 100 ml solution. Adsorption results have been given in figure 4. The result indicated that the adsorption of mercury increased with increasing the adsorbent dose. After reaching the equilibrium it showed reverse relationship with adsorbent due to electrostatic interactions, interference between binding sites and higher dose of adsorbent (Salim *et al.*, 2007; Salim *et al.*, 2008). Finally the adsorbent dose of 200, 400 and 600 mg in 100 ml solution is sufficient for the maximum removal (98 percent) from aqueous solution of mercury of (1, 5 and 10) mg l⁻¹. Since, any further adsorbent dose not taking place beyond this dose of adsorbent used.

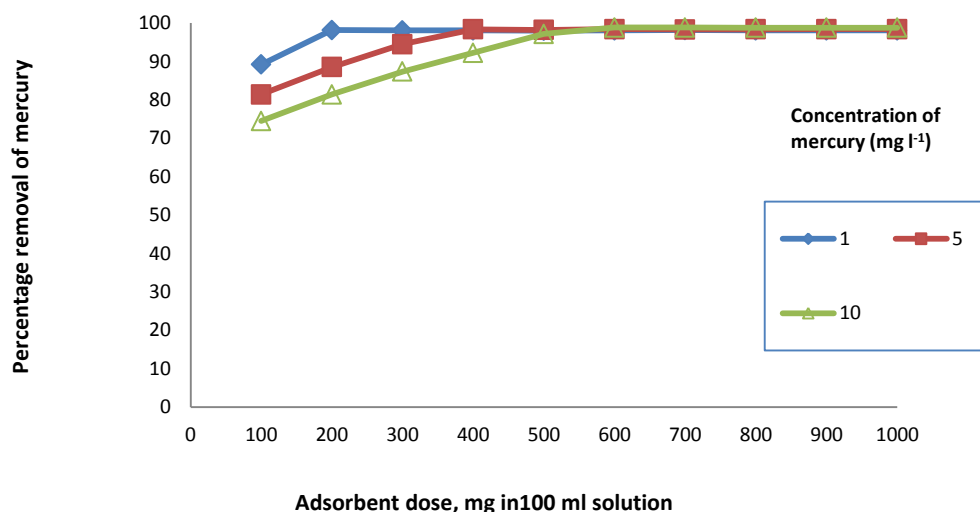


Figure 4. Effect of adsorbate concentration and adsorbent dose on the removal of mercury

3.4. Effect of Temperature

The study of effect of temperature on adsorption process is an important aspect in waste water treatment. Temperature effect for adsorption mechanism is defined as heat of adsorption (ΔH). Adsorption reactions are normally exothermic in nature. It may be explained on the basis of rapid increase in the rate of adsorption from the surface of adsorbent.

The effect of temperature on mercury concentration of 10 mg l⁻¹ with a fix amount of adsorbent dose of 600 mg per 100 ml solution was performed by this process of investigation. This study was carried out at three temperatures varied from (303, 313 and 323) K under identical condition of 2 hours duration of contact time. The results are shown in figure 5. It is clear from the figure that the adsorption was almost greater at lower temperature, while adsorption decreases with increasing the temperature. The increase in adsorption with decrease in temperature indicates exothermic nature of the adsorption process.

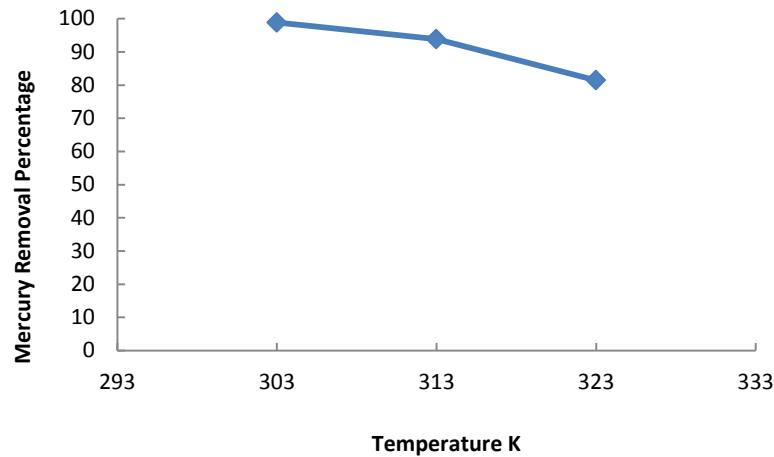


Figure 5. Effect of Temperature on the removal of mercury

3.5 Adsorption kinetics

The kinetics of mercury adsorption data were analyzed using pseudo first order and pseudo second order kinetic models which are proposed by Lagergreen (Lagergreen S., 1898).

(I) The pseudo-first order model is generally expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

Where q_e and q_t in (mg g^{-1}) are the adsorption capacity at equilibrium and at time t , respectively and k_1 (h^{-1}) is the Lagergreen rate constant of the pseudo first order kinetics. On the integrating equation 2 between the limits, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$, it becomes

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

The plot of $\log (q_e - q_t)$ versus t (figure 6), gave a linear relationship from which the value of k_1 can be calculated from the intercept of the plot. The values of k_1 and R^2 have been given in table 2.

(II) The pseudo second order model is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

Where k_2 ($\text{l mg}^{-1} \text{h}^{-1}$), is the rate constant of the pseudo second order adsorption ($\text{l mg}^{-1} \cdot \text{h}^{-1}$). On the integrating equation 4 from the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$, it becomes

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

The plot of (t/q_t) versus t (figure 7) gave a linear relationship from which k_2 can be calculated from the intercept of the plot. The value of k_2 and correlation coefficient R^2 have been given in table 2.

Table 2. Values of first order rate constant k_1 , second order rate constant k_2 and correlation coefficient R^2

First order rate constant		Second order rate constant	
k_1 (h^{-1})	R^2	k_2 ($\text{l mg}^{-1} \cdot \text{h}^{-1}$)	R^2
1.422	0.996	0.135	0.997

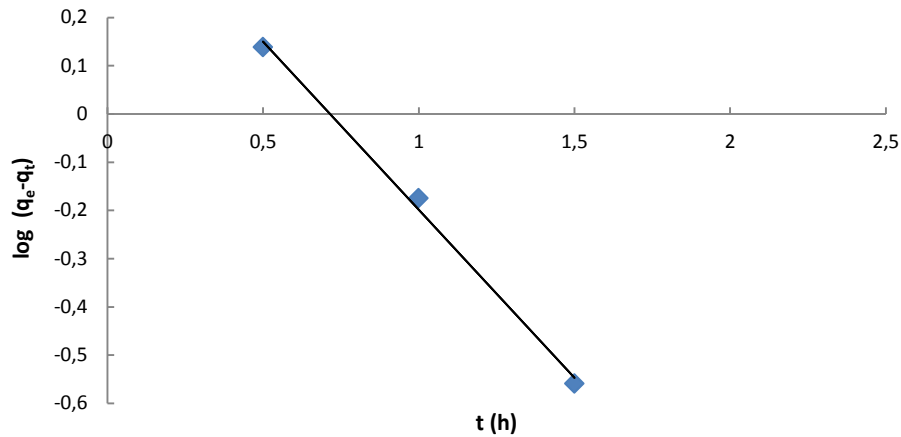


Figure 6. Pseudo first order adsorption

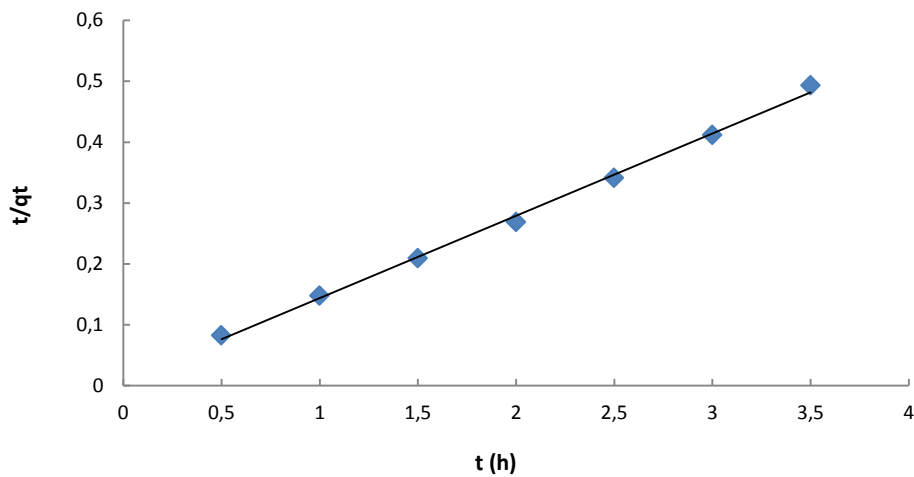


Figure 7. Pseudo second order adsorption

4. Conclusions

On the basis of present study, it is concluded that, fly ash could be used as low cost adsorbent for the removal of mercury. The experimental results were based on five parameters; contact time, pH, adsorbate concentration of mercury, adsorbent dose of fly ash and temperature. These showed that the adsorption was increased with increasing the adsorbent dose and then decreases. For contact time parameter maximum removal was found 74 percent from 10 mg l⁻¹ of mercury concentration on to 100 mg per 100 ml of adsorbent dose, the effect of pH for maximum removal was found to be 90 percent at pH 10 for initial concentration of mercury (10 mg l⁻¹). The effect of adsorbate and adsorbent doses were found that 200, 400 and 600 mg per 100 ml of adsorbent solutions were sufficient to maximum removal of initial concentration (1, 5 and 10) mg l⁻¹ of mercury (98 percent), at equilibrium conditions i.e., 2 hours duration of contact time, pH-10 and 303 K temperature. The effect of temperatures showed that maximum mercury removal was 89 percent at 303 K, However, variety of adsorbent media including activated carbon and other adsorbents are available but some of them are costly and some having negative environmental hazardous impact therefore, fly ash is economical feasible and easily available adsorbent which could be used for the removal of mercury. It is also found that experimental data are well fitted with adsorption kinetics of pseudo first order and pseudo second order rate constant.

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