Defence Science Journal, Vol. 54, No. 4, October 2004, pp. 537-548

Low-cost Adsorbents for the Removal of Mercury (II) from Aqueous Solution–A Comparative Study

Ajay Kumar Meena, G.K. Mishra, Satish Kumar, and Chitra Rajagopal
Centre for Fire, Explosive & Environment Safety, Delhi–110 054

and

P.N. Nagar
University of Rajasthan, Jaipur–302 004

ABSTRACT

The establishments of the Ministry of Defence, specifically ordnance factories and public sector undertakings (like Bharat Electronics Ltd), carry out operations like electroplating, metal/surface finishing, solid-state wafer processing, and initiatory manufacturing (lead azide, mercury fulminate), which generate waste water contaminated with hazardous heavy metals. Mercury and its compounds are known to be highly toxic, both for the living organisms and the environment. To protect public health, a regulatory discharge standard of mercury, as low as 0.01 mg/l, has been imposed and is expected to be even stricter in the future. A promising method for effective mercury discharge control is to employ suitable adsorbents for the removal of mercury from the contaminated aqueous stream.

This paper describes the effectiveness of low cost and locally available, untreated and chemically-treated adsorbents for the removal of mercury from the aqueous solution. Their effectiveness has been compared with that of chemically-treated granular activated carbon. Treated sawdust and untreated weathered coal were found to be the most suitable low-cost adsorbents in addition to treated granular activated carbon for the removal of mercury from aqueous solution. Under the optimised conditions, ie, adsorbent dose 10 g/l, p*H* 6, contact time 48 h, and initial concentration of mercury 3 mg/l, the removal of mercury was found to be 99.8 per cent, 99.8 per cent, and 99.7per cent, using treated granular activated carbon, treated sawdust, and untreated weathered coal, respectively.

The adsorption parameters were determined using both Langmuir and Freundlich isotherm models. Surface complexation and ion exchange were the major removal mechanisms involved. The adsorption isotherm studies clearly indicated that the Langmuir model is in good agreement with the experimental data on the adsorptive behaviour of mercury on treated granular activated carbon, whereas, the experimental data on adsorptive behaviour of mercury on weathered coal and treated sawdust follow both Langmuir and Freundlich isotherm models. The paper presents the results of the experimental studies as well as the model parameters.

Keywords: Hazardous heavy metals, waste water, environmental pollution, toxicity, mercury, adsorbents, water contamination

---

Revised 01 April 2004

1. INTRODUCTION

The establishments of the Ministry of Defence, specifically ordnance factories and public sector undertakings like Bharat Electronics Ltd, carry out operations like electroplating, metal/surface finishing, solid-state wafer processing, and initiatory manufacturing (lead azide, mercury fulminate) which generate waste water contaminated with hazardous heavy metals. The concentrations of some of the toxic heavy metals like Cr(VI), Hg(II), Pb(II), As(III), etc are higher than the permissible discharge levels. Therefore, an appropriate treatment is required before their released into the environment. Mercury is generally considered to be one of the most toxic metals found in the environment[1]. Mercury occurs primarily in two forms–inorganic mercury and organic mercury. Inorganic mercury includes inorganic salts of mercury, eg, chloride, bromide, sulphide, and sulphate whereas organic mercury includes methyl mercury.

Methyl mercury causes deformities in the offspring and teratogenic effects (mainly affecting the nervous system). Children suffer from mental retardation, cerebral palsy, and convulsions. The harmful effects of methyl mercury on aquatic life and human beings was amply brought out by the Minamata episode in Japan[2]. Once mercury enters the food chain, progressively more and more accumulation of mercury compounds takes place in human beings and animals.The major sources of mercury pollution in the environment are industries like chlor-alkali, paints, pulp and paper, oil refining, rubber processing, fertilizers[3,4], batteries, thermometers, fluorescent light tubes, and high intensity street lamps, pesticides, cosmetics and pharmaceuticals[5]. According to the Bureau of Indian Standards (BIS), the limit for mercury(II) for discharge[6] into inland surface water is 10 μg/l and for drinking water[7], it is 1 μg/l.

Mercury also brings about genetic defects, causing chromosome breaking and interference in cell division, resulting in abnormal distribution of chromosomes[8]. Mercury causes impairment of pulmonary and kidney function, chest pain and dyspnea [9,10]. Toxicity of mercury is much greater than any other substance, therefore, it is essential to remove mercury from waste water before it is released into the environment.

The conventional methods for the removal of mercury from waste water include electrolysis reduction process, sulphide precipitation, ion exchange, alum and iron coagulation, and adsorption on activated carbon[11]. Efficient and cost-effective removal of mercury from waste water resulted in a search for non-conventional adsorbents like fly ash[2], dispersed iron oxide, activated carbon fibres[12], waste rubber[13], polymerised onion skin[14], peat moss[15], polymerised sawdust[16], cellulose[17], aqueous solution of waste Fe (III) / Cr (III) hydroxide, rice husk[18], agricultural waste and by-products[11,19,20], tree bark[14], peanut skin, citrus skin, coffee husk[21], coconut shell, and peanut hull carbon, ozonised granular activated carbon[22], heat-treated and sulphurised granular activated carbon[23], and steam-sulphurised granular activated carbon prepared from bagasse pith[24].

The sawdust (particle size range 40-70 mesh) is a commonly available and inexpensive by-product of timber industry and contains various organic compounds with poly-phenolic groups, that might be useful for binding heavy metal ions. The adsorption of mercury ions on modified sawdust, however, has not been carried out in detail. The discarded weathered coal as a by-product is in abundance in thermal power plants, and is dumped in the open for long time. As its calorie value is low, its use as a fuel is limited. The granular activated carbon when impregnated with suitable chemicals, offers scope for physical and chemical sorption of mercury ions.

In the present work, during search for a cheap, readily available and effective adsorbent material, sawdust has been identified as a potentially attractive adsorbent for the treatment of mercury-contaminated aqueous solutions/waste water after pre-treatment with 2.0 N $NaOH$ and 0.2 N H_2SO_4 to remove lignin content and to enhance the porosity. Since there are huge deposits of sawdust around saw mills, there is a great potential for its utilisation in water pollution control. A number of researchers have reported the use of sawdust for treatment of toxic, heavy metal-contaminated aqueous solutions[25-28].

The discarded weathered coal is another cheap and readily available adsorbent material found suitable for the removal of mercury from contaminated aqueous solution/waste water. The impregnated granular activated carbon has also been used as an adsorbent for the adsorptive removal of mercury from aqueous solution/ waste water for comparative evaluation.

2. EXPERIMENTAL PROCEDURE

The screening studies were conducted to enable comparative evaluation of various types of adsorbents for the removal of mercury from aqueous solution/ waste water. The adsorbents studied were–treated and untreated granular activated carbon, treated and untreated sawdust, polymerised sawdust, weathered coal, and mustard husk. The experiments for screening studies were carried out using stoppered conical flasks containing 100 ml of 4 mg/l mercury test solution and 1 g of the adsorbent material. The flasks containing the test solution and the adsorbent were placed in a thermostatic mechanical shaker for 24 h contact time at 35 °C.

On the basis of the screening studies, the most promising adsorbents selected were treated granular activated carbon, treated sawdust, and weathered coal, which were used for further experiments to study the effect of other parameters. The experiments were carried out in a phased manner as given below:

Phase 1: Effect of initial concentration

Phase 2: Effect of adsorbent dosage

Phase 3: Effect of contact time

Phase 4: Effect of p*H*

2.1 Experimental Conditions for Phases 1 to 4

- Volume of sample taken for each experiment = 100 ml
- p*H* range = 2 to 12
- Initial concentration range (mg/l) (based on analysis of actual plant effluent samples) = 0.5 to 4.0
- Contact time (h) = 24, 48, 72
- Adsorbent dose (g/100 ml) = 0.3, 0.5, 0.8 and 1.0

The results of these studies were used to obtain the optimum conditions for the maximum removal of mercury from the aqueous solution.

3. MATERIALS & METHODS

3.1 Instrumentation

The GBC 932 AA atomic absorption spectrometer operating with cold vapour method (hydride generator FS 3000) was used to analyse the concentration of mercury(II). The minimum detection limit was equal to or less than the EPA requirement. Three standard solutions with concentrations of mercury(II) in the linear range of the instrument were used to construct each calibration curve. During analysis of the samples for mercury(II) concentration, those samples in which the concentration of mercury(II) was observed beyond the linear range of the references were diluted to appropriate concentrations. All measurements were repeated thrice, and those results in which the standard deviations were found greater than 0.1 mg/l were not accepted.

The p*H* measurements were performed with a controlled p*H* analyser (LABINDIA). The p*H* meter was standardised using buffer solutions of p*H* values: 4.00, 7.00, 9.00, and 12.00.

A mechanical shaker (of WIDSONS SCIENTIFIC make) was used for all the adsorption experiments for agitating the sample for a desired contact time.

3.2 Test Solution

The synthetic stock solution of mercury (II) was prepared by dissolving required quantity of Analar-grade mercuric chloride ($HgCl_2$) in the demineralised distilled water. The stock solution was further diluted with demineralised distilled water to the desired concentration for obtaining the test solutions.

3.3 Preparation of Adsorbents

3.3.1 *Treated Sawdust*

Sawdust contains lignin, which results in poor adsorption and red colouration of the treated water; therefore, sawdust was first chemically treated to remove the lignin before using it for the adsorption study.

The raw sawdust (particle size range 40-70 mesh) was immersed in 2N $NaOH$ aqueous solution for 8 h. Thereafter, it was washed several times with distilled water to remove the lignin content and excess of $NaOH$ and then dried. It was observed that a dark-red solution was generated during this treatment, which indicated the removal of lignin from the adsorbent material. The sawdust was repeatedly washed with double-distilled water till no red colouration was observed. It was then immersed in 0.2N H_2SO_4 for 8 h to remove the traces of alkalinity and other impurities. The acid-treated sawdust was again thoroughly washed with double-distilled water to remove the excess of H_2SO_4 and other colouring materials till the wash-found water was colourless. After this, the treated sawdust adsorbent material was dried in the sun and stored in a dessicator for use as an adsorbent. The treated sawdust material was found to be lighter in colour and weight.

3.3.2 *Treated Granular Activated Carbon*

The untreated granular activated carbon has poor adsorptive removal efficiency for mercury ions because it lacks appropriate chemical functional groups on its surface. Chemical treatment is essential to introduce a suitable functional group (S^{2-},SH^-) on its surface for the enhancement in adsorption capacity[29].

Coconut-based granular activated carbon (99.5 g) was immersed for 24 h in the minimum quantity of distilled water containing Na_2S (0.5 g). The mixture was heated to remove the moisture and further dried at 110 °C in an oven for 4 h. The dried sample was washed with distilled water several times till it gave negative test for sulphide. The washed sample was again dried at 110 °C for 4 h and stored in a dessicator for use.

3.3.3 *Weathered Coal*

The weathered coal was used as an adsorbent material without any pre-treatment.

3.4 Batch Experiments

Batch adsorption studies were carried out using stoppered conical flasks containing required amount of test solution and adsorbent material. The flasks containing the test solution and the adsorbent were placed in a thermostatic mechanical shaker at 35 °C for the required contact time. The contents were centrifuged and filtered through Whatman filter paper No. 41. The unadsorbed mercury in the filtrate was estimated by GBC 932 AA atomic absorption spectrophotometer, using the cold vapour atomic absorption method[30].

4. RESULTS & DISCUSSION

4.1 Effectiveness of Adsorbent materials

Eight different adsorbents, namely untreated granular activated carbon, mustard husk, sawdust, weathered coal, carbon aerogel, treated sawdust, polymerised sawdust, and treated granular activated carbon were used in the screening experiments. Table 1 gives the percentage removal of mercury by various adsorbents. From this, it can be seen that the percentage removal is appreciably better with treated sawdust, treated granular activated carbon, and weathered coal than with the other adsorbents. In view of the poor mercury removal efficiencies with sawdust, polymerised sawdust, untreated granular activated carbon, and carbon aerogel, it was decided to continue the remaining sets of experiments with treated sawdust, treated

Table 1. Results of screening studies for selection of adsorbents

Adsorbents	Weathered coal	GAC	Sawdust	Polymerised sawdust	Treated sawdust	Treated GAC	Mustard husk	Carbon aerogel
Removal of mercury (%)	98.1	76.0	68.3	95.0	99.5	99.6	56.2	94.8

Initial Concentration: 4 mg/l, contact time: 24 h, adsorbent dose: 1 g, and sample volume: 100 ml granular activated carbon, and weathered coal as adsorbents.

The observed high removal efficiencies with treated granular activated carbon may be attributed to chemical functional group $-S^{2-}/-SH^-$ on the surface of treated granular activated carbon, which has more chemical affinity for mercury(II). Further, the treated sawdust is much more effective than untreated sawdust for the removal of mercury(II) because of higher porosity and the moderate ion-exchange capacity of treated sawdust compared to untreated sawdust. In this study, weathered coal had also shown promising adsorptive potential for mercury (II), which may be attributed to the presence of peripheral exchanging functional groups like carboxylic and hydroxyl groups on its surface[31].

4.2 Effect of Initial Mercury Concentration

The Fig. 1 depicts the percentage removal of mercury using treated granular activated carbon, treated sawdust, and weathered coal for adsorbent dose (0.8 g) and contact time (48 h). The treated granular activated carbon gives the best results, ie, nearly 100 per cent removal of mercury to 1 mg/l level, after which it decreases slightly to about 99.7 per cent for higher concentrations. The treated sawdust is highly effective up to 1 mg/l, after which the percentage removal of mercury decreases gradually to about 99.3 per cent at 4 mg/l level. Weathered coal shows a gradual decrease in percentage removal of mercury from lower initial concentration to higher initial concentration of mercury, ie, from 99.6 per cent to 99.2 per cent for 0.5 mg/l to 4.0 mg/l level of initial mercury concentration.

At lower initial concentrations, sufficient sites are available for the adsorption of the mercury molecules. Therefore, the fractional adsorption is independent of initial concentration. However, at higher concentrations of mercury, the number of mercury ions is relatively higher compared to the availability of adsorption sites. Hence, the percentage removal of mercury depends on the initial concentration and decreases with the increase in the initial concentration.

4.3 Effect of Adsorbent Dosage

The percentage removal of mercury is seen to increase with increasing adsorbent dose. Figure 2 shows the comparative behaviour of the selected adsorbents with increasing adsorbent dosage. It is observed that there is a sharp increase in percentage removal of mercury with adsorbent dose for weathered

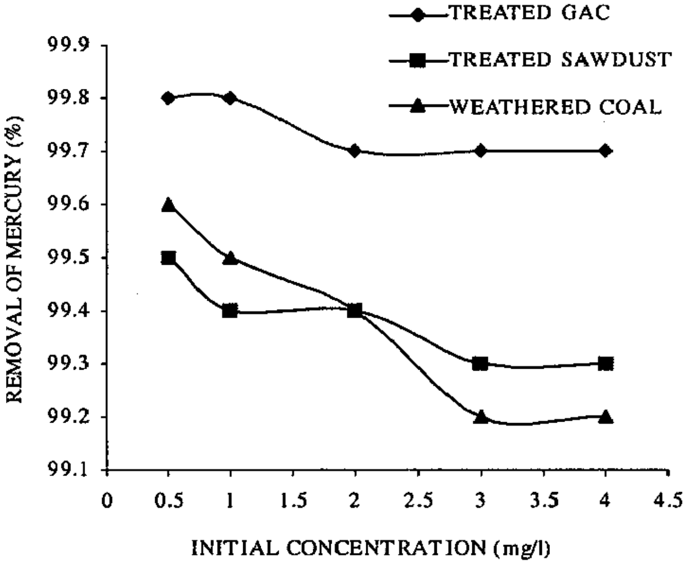

Figure 1. Effect of initial concentration on percentage removal of mercury for different adsorbents. Adsorbent dose = 0.8 g/100 ml, and contact time = 48 h.

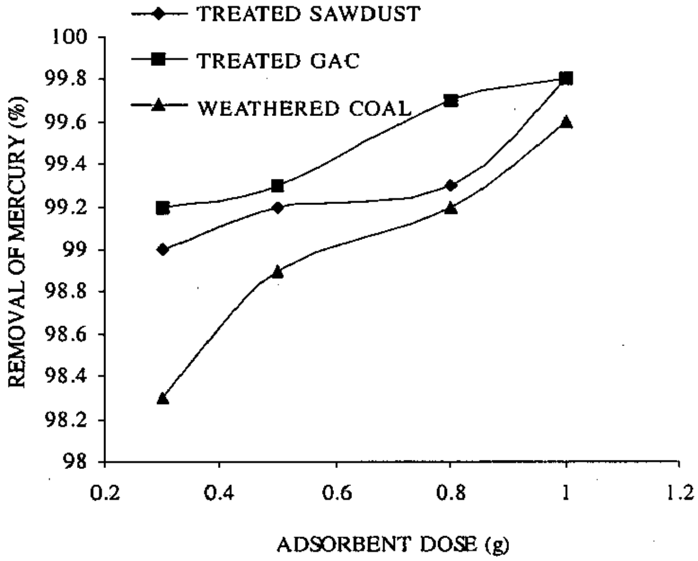

Figure 2. Effect of adsorbent dosage on percentage removal of mercury for different adsorbents. Contact time = 48 h, and initial concentration = 3 mg/l.

coal, from about 98.2 per cent for 0.3 g dose to nearly 99.5 per cent for 1 g dose. The treated sawdust does not show much variation for low adsorbent dosage but increases gradually to 100 per cent for 1 g dose. The treated granular activated carbon shows 99.1 per cent to 99.8 per cent removal over the entire range of adsorbent dosage studied.

It is apparent that the percentage removal of mercury increases sharply with increase in the dosage of the adsorbent due to greater availability of the active sites or surface area at higher doses of the adsorbent. This is certainly a capacity effect.

4.4 Effect of Contact Time

The Fig. 3 shows the comparative percentage removal of mercury using 0.8 g/100 ml each of treated granular activated carbon, treated sawdust, and weathered coal for an initial concentration of 3 mg/l for different contact times. It was observed that in all cases, the percentage removal was comparatively lower for 24 h contact time, with increasing mercury removal efficiencies at higher contact times. In the case of treated granular activated carbon, the overall percentage efficiencies at any contact time were the highest. The treated sawdust showed lower removal percentage than the treated granular activated carbon and weathered coal for 24 h contact time but the rise in percentage removal with increasing contact time is steep, showing nearly 99.1 per cent removal beyond 48 h. On the other hand, percentage removal with treated sawdust and untreatedweathered coal increases gradually with increase in contact time, reaching nearly 100 per cent removal only at around 72 h.

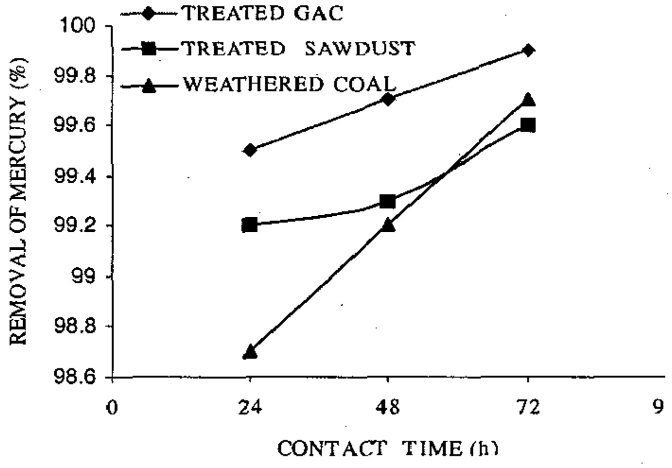

Figure 3. Effect of contact time on percentage removal of mercury for different adsorbents. Adsorbent dose = 0.8 g/100 ml, and initial concentration = 3 mg/l.

It is evident from the experimental results that the contact time required to attain equilibrium depends on the initial concentration of mercury. For the same concentration, the percentage removal of mercury increases with increase of contact time till equilibrium is attained. The optimal contact time to attain equilibrium with all the three adsorbents were experimentally found to be about 48 h. The rise in percentage removal of mercury beyond 48 h in not appreciable.

4.5 Effect of p*H*

The p*H* is one of the most important parameter controlling the adsorption of mercury from waste water and aqueous solutions. Figure 4 shows the effect of p*H* on mercury removal efficiencies of all the three adsorbents. These studies were conducted at a constant initial mercury concentration (3 mg/l), adsorbent dose 0.8 g/100 ml, and contact time (48 h) for all the three adsorbents.

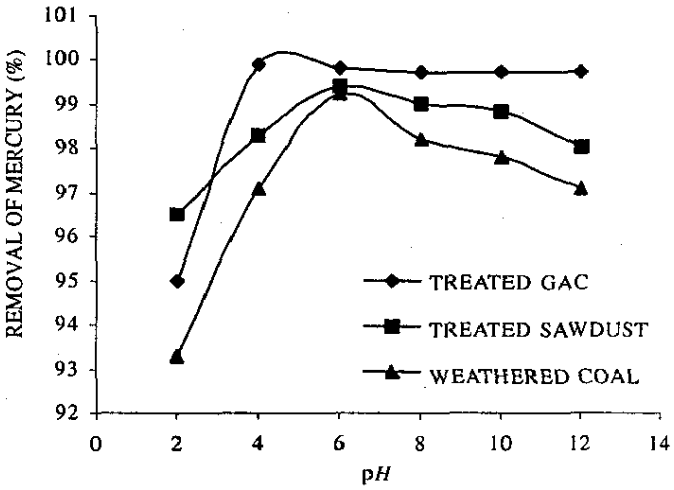

Figure 4. Effect of p*H* on percentage removal of mercury for different adsorbents. Adsorbent dose = 0.8 g/100 ml, contact time = 48 h, and initial concentration = 3 mg/l.

The percentage adsorption increases with an increase in the pH to attain a maximum at pH 6 and thereafter, it decreases with further increase in pH. The maximum removal of mercury at pH 6 was found to be nearly 100 per cent, 99 per cent and 98.6 per cent for treated granular activated carbon, weathered coal, and treated sawdust, respectively. These results indicate that treated granular activated carbon, weathered coal, and treated sawdust could be satisfactorily used at existing pH of the test solution.

The lower pH values result in the protonation of adsorbent surface, which leads to the extensive repulsion of Hg^{2+} ions. This results in a decrease in mercury(II) adsorption. With increase of pH from 2.0 to 6.0, the mercury exists as mercuric hydroxide [$Hg(OH)_2$] in the medium and surface protonation of adsorbent is minimum, leading to the enhancement of Hg^{2+} ions adsorption.

The influence of the pH on mercury(II) adsorption by treated granular activated carbon, weathered coal, and treated sawdust is noticed in the present study. Based on the previous studies, it has been reported that the adsorption decreases at acidic pH due to the lower adsorption of $HgCl_2$ species (present at acidic pH) as compared to $Hg(OH)_2$ species (present at pH 6). This hypothesis is supported by the results obtained in the present study, because the amount of mercury(II) adsorbed at pH 6 is much greater than that adsorbed at pH 2 . The decreased adsorption at pH 2 may be due to the lesser extent of the reduction of $HgCl_2$ to Hg_2Cl_2 at this pH as a result of the elevated HCl concentration in the medium.

On increasing the pH from 2, the percentage removal of mercury increased and became maximum at pH 6. This implies that $Hg(OH)_2$ species may be retained in the micropores of the adsorbent particles by chemisorption, involving surface complexes[3].

Because of the chemical treatment of sawdust with H_2SO_4 and $NaOH$ and granular activated carbon treated with Na_2S, the functional groups, such as $C{-}OH^+$, $C{-}ONa^+$, $C{-}SH$ are assumed to be present on the surface of the above adsorbents. When mercury (II) is present in the adsorptive solution, the following surface complexes may be formed:

$$2C_xOH^+ + Hg^{2+} \rightarrow (C_xO)_2\,Hg^{2+} + 2H^+$$

$$2C_xONa^+ + Hg^{2+} \rightarrow (C_xO)_2\,Hg^{2+} + 2Na^+$$

$$2\,C_xSH + Hg^{2+} \rightarrow (C_xS)_2\,Hg^{2+} + 2H^+$$

These surface complexes would enhance the chemisorption of mercury on the surface of the adsorbent and result in the observed increased adsorption capacity as compared to untreated adsorbents.

5. ADSORPTION ISOTHERMS

The adsorption studies were conducted at the fixed initial concentration of mercury by varying adsorbent dosage. The equilibrium data obtained was analysed in the light of Langmuir and Freundlich isotherms.

The Freundlich equation is given by

$$x/m = K\ C_e^{1/n}$$

Taking the logarithmic from of the equation, one has:

$$\log x/m = \log K + 1/n \log C_e$$

The Langmuir equation is given by

$$x/m = abC_e\ /\ (1+ bC_e\ )$$

or

$$x/m = (1/ab).\ (1/C_e) + 1/a$$

where x/m is the amount of mercury adsorbed per unit mass of adsorbent in mg/g, C_e is the equilibrium concentration of mercury in mg/l, K_e and n are Freundlich constants, a is a Langmuir constant, which is a measure of adsorption capacity expressed in mg/g, and b is also Langmuir constant, which is a measure of energy of adsorption expressed in l/mg.

The parameters a and b have been calculated from the slope and the intercept of the plots.

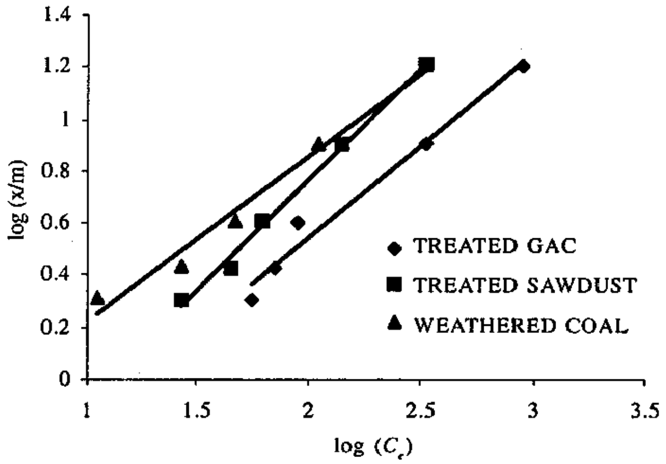

Figure 5. The Freundlich isotherms of mercury for various adsorbents. Amount of adsorbent = 0.8 g, and contact time = 24 h.

The Fig. 5 gives the Freundlich adsorption isotherm plot of log *x*/*m* versus log C_e. The values of K_e and 1/*n* obtained from intercept and slope of the plot are given in Table 2.

The Langmuir adsorption isotherm plot for *m*/*x* versus $1/C_e$ is shown in Fig. 6 and the plots show two distinct regions, one for low $1/C_e$ values, up to about 25 l/mg and another for higher $1/C_e$ values. This distinct behaviour for the two different $1/C_e$ ranges is especially noticeable in the case of treated sawdust. The essential characteristics of the Langmuir isotherm can be described by a separation factor or equilibrium constant R_L, which is defined as

$$R_L = 1 / (1 + bC_i)$$

where C_i is the initial concentration of mercury (mg/l) and *b* is the Langmuir constant, which indicates the nature of adsorption. The separation factor, R_L, indicates the isotherm shape and whether the adsorption is favourable or not, as per the criteria given below.

R_L Value	**Adsorption**
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The values of Langmuir constants *a*, *b* and R_L are presented in Table 2. Since R_L values lie between 0 and 1 for all the three adsorbents studied, it is seen that the adsorption of mercury is favourable.

The adsorption capacity, as indicated by value of *a* is seen to be maximum for treated granular activated carbon, ie, 122.2 mg/g, followed by weathered coal, with an adsorption capacity of 45.7 mg/g, and treated sawdust, with a much lower capacity of 20.6 mg/g. The energies of adsorption, as indicated by *b* are seen to be the highest for treated sawdust, followed by treated granular activated carbon, and weathered coal, in that order. A comparison of the Freundlich adsorption isotherms for the three adsorbents shows that *n* is maximum for weathered coal and minimum for treated sawdust, K_e, seen to be higher for weathered coal and the least for treated sawdust. This gives a similar inference as that obtained from the Langmuir isotherms.

Table 2. The values of Langmuir and Freundlich isotherm constants for adsorption of mercury

Adsorbent	Langmuir constants				Freundlich constants		
	a (mg/g)	*b* l/mg	R^2	R_L	K_e	*n*	R^2
Treated GAC	122.20	0.51	0.98	0.32	0.42	1.42	0.97
Treated sawdust	20.63	1.05	0.99	0.24	0.39	1.17	0.99
Weathered coal	45.75	0.50	0.98	0.33	0.95	1.57	0.98

Amount of adsorbent = 0.8 g/100 ml, and contact time = 24 h

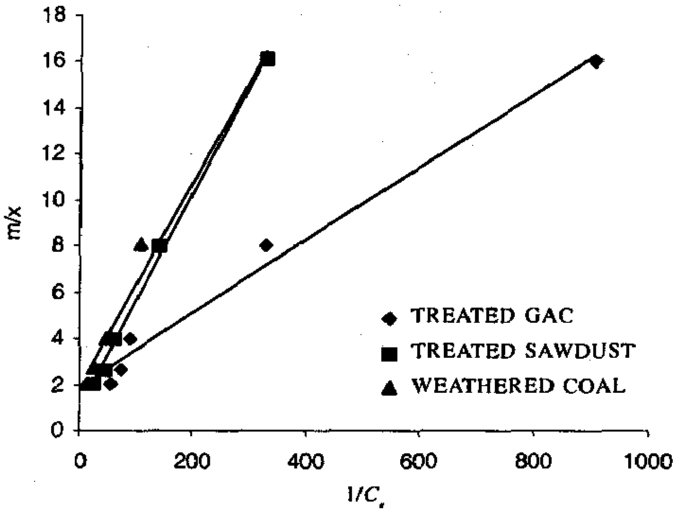

Figure 6. Langmuir isotherms of mercury for various adsorbents. Amount of adsorbent = 0.8 g, and contact time = 24 h.

On the basis of regression analysis of the experimental data on the adsorptive behaviour of mercury on treated granular activated carbon, weathered coal, and treated sawdust, it may be inferred that the adsorption behaviour of mercury on treated granular activated carbon is in good agreement with the Langmuir model. These can be attributed to the formation of monolayer coverage on the surface of treated granular activated carbon with minimal interaction among molecules of the substrate, immobile and localised adsorption, and all sites having equal adsorption energies. Whereas, the adsorptive behaviour of mercury on untreated weathered coal and treated sawdust satisfies not only the Langmuir assumptions but also the Freundlich assumptions, ie, multilayer formation on the surface of the adsorbent with an exponential distribution of site energy.

The differences in the extent of adsorption of mercury are associated with the chemical state of the metals in the aqueous solutions being treated. In the case of metal halides like $HgCl_2$, solubility can also play an important role. Usually, the greater part of $HgCl_2$ is found undissociated. For example, in a 3×10^{-2} molar $HgCl_2$ solution, less than 2 per cent undergoes primary dissociation.

$$HgCl_2 = [HgCl]^+ + Cl^-$$

and the extent of secondary dissociation

$$[HgCl]^+ = Hg^{2+} + Cl^-$$

is negligibly small[32]. The existence of dimeric $HgCl_2$ in water solutions has also been hypothesised[33]. The stability constant of the equilibrium

$$2HgCl_2 = (HgCl_2)_2$$

at various temperatures in water is known ($\log k_{25} = -0.55$). Therefore, it is also proposed that mercury (II) may be adsorbed on the activated carbon via a mechanism of $HgCl_2$ molecular adsorption with the subsequent reduction of the $HgCl_2$ due to the presence of phenol and hydroquinone groups on the carbon surface[34,35].

$$2(C{-}OH) = 2HgCl_2 \leftrightarrow 2(C = O) = HgCl_2 = 2HCl$$

A recent electron microscopy study confirmed the presence of Hg^+ and Cl^- on the surface of activated carbon in contact with $HgCl_2$, which supports the reduction mechanism given below:

$$2(C{-}SH) + 2HgCl_2 \leftrightarrow 2\ (C{=}S) + HgCl_2 + 2HCl$$

Prior to the above studies, Sanchez[22], *et al.* had discussed the possibility that π electrons of the basal plane may be involved in the reduction of Hg on the adsorbent surface. The basicity of adsorbents could be due to the presence of basic oxygen containing functional groups (eg, pyrones or chromines) and graphene layers that act as Lewis base and form electron donor-acceptor (EDA) complexes with H_2O molecules. The latter basic sites are located at π electron-rich regions within the basal planes of adsorbent crystallites, away from the crystallite edge. In authors' view, this delocalised π electron system ($-C\pi$) can act as a reduction centre of different species:

$$2e^- + 2Hg(OH)_2 \leftrightarrow Hg_2(OH)_2 + 2OH^-$$

Thus, the decrease in mercury (II) adsorption with more oxygen (electron-withdrawing) functional groups on the adsorbent surface may be due to: (i) a reduction in the basicity of the adsorbent because of decrease in its surface electronic density and weakening of dispersion interaction between adsorbent surface and $Hg(OH)_2$, and (ii) a decrease in the reductive properties of the adsorbent which may cause decrease in the $Hg(OH)_2$ adsorbed.

6. CONCLUSIONS

Based on the above experimental studies, the following conclusions have been drawn:

(a) Treated granular activated carbon, weathered coal, and treated sawdust showed 99.9 per cent, 99.8 per cent, and 99.7 per cent adsorptive removal of mercury under optimised conditions of p*H* 6 and dosage 8 g/l (0.8 g/100 ml) for 3 mg/l mercury aqueous solution in 48 h, respectively.

(b) The adsorption is p*H*-dependent and the maximum adsorption occurs at p*H* 6.

(c) The Langmuir model is in good agreement with the experimental data on the adsorptive behaviour of mercury on treated granular activated carbon, whereas, the experimental data on adsorptive behaviour of mercury on weathered coal and treated sawdust follow both the Freundlich model and the Langmuir model.

(d) These experimental studies on low-cost adsorbents would be quite useful in developing an appropriate technology for the removal of mercury from contaminated effluents generated by various prcessing industries.

ACKNOWLEDGEMENTS

The authors are grateful to Shri A.K. Kapoor, the then Director, Centre for Fire, Explosive and Environment Safety (CFEES), Delhi, for providing encouragement and facilities for carrying out this study. Thanks are also due to Shri A.S. Rawat, Senior Technical Assistant 'C', for carrying out analysis of the samples by atomic absorption spectrophotometer.

REFERENCES

1. Serpone, N.; Borgarello, E. & Pelizzti, E. Photoreduction and photodegradation of inorganic pollutants. *In* Photocatalysis and environment, edited by M. Schiavello. Kluwer Academic, Derdeeht, 1988. 527.
2. WHO Environmental Health Criteria 118: Inorganic mercury. Geneva, World Health Organisation, 1991. 68p.
3. Kapoor. A. & Viraghavan, T. Adsorption of mercury from waste water by fly ash. *Ads. Sci Tech.*, 1990, **9**, 130.
4. Namasivayam, C. & Periasamy, K. Bicarbonate-treated peanut hull carbon for mercury (II) removal from aqueous solutions. *Water Resources,* 1993, 27, 1663.
5. Krishnan, A.K. & Anirudhan, T.S. Removal of mercury (II) from aqueous solutions and chlor-alkali industry effluent by steam-activated and sulphurised-activated carbons prepared from bagasse pith: Kinetics and equilibrium studies. *J. Hazardous Mater.*, 2002, **92**, 161-83.
6. Bureau of Indian Standards. Tolerance limits for industrial effluents prescribed by Bureau of Indian standards. BIS Standard No IS-2490, 1981.
7. Tolerance limits for drinking water prescribed by Bureau of Indian standards. BIS Standard No IS-10500, 1991.
8. Sharma, P.D. Ecology and Evironment. 2001.
9. Berglund, F. & Bertin, M. Chemical fallout, Springfield, IL Thomas., 1969.
10. WHO Environmental Health Criteria 101: Methyl mercury. Geneva, World Health Organisation, 1990. 68p.
11. Roberts, E.J. & Rowland, S.P. *Environ. Sci. Tech.*, 1973, **7**, 552.
12. Kamko, K. *Carbon*, 1988, **26**, 903.
13. Knocke, W.R. & Homphil, L.H. Mercury (II) sorption by waste rubber. *Water Resources*, 1981, **15**, 275.
14. Kumar, P. & Dara, S.S. Binding heavy metal ions with polymerised onion skin. *J. Polymer Sci.*, 1981, **19**, 397.
15. Coupal, B. & Lalacette, J.M. The treatment of waste water with peat moss. *Water Resources,* 1976, **10**, 1071.

16. Raji, C. & Anirudhan, T.S. Removal of *Hg* (II) from aqueous solution by sorption on polymerised sawdust. *Ind. J. Chem. Tech.*, 1996, 3, 49.

17. Navarvo, R.R.; Sumi, K.; Fugir, N. & Matsumuru, M. Mercury removal from waste water using porous cellulose carrier modified with polyethylene amine. *Water Resources,* 1996, **30**, 2488.

18. Srinivasan, K.; Balasubramanium, N. & Ramakrishana, T.V., *Ind. J. Environ. Health*, 1988, **30**, 376.

19. Jahagirdar, D.V. & Nigal, J.N. Adsorption of *Cd*(II) and *Pb*(II) on agricultural by-products. *Asian J. Chem.*, 1997, **9**, 122.

20. Jumle, R. *et al.* Studies in adsorption of some toxic metal ions on citrus sinensis skin and coffea arabica husk: Agricultural by-products. *Asian J. Chem.*, 2002, **14**(3-4), 1257-260.

21. Ravi, J.; Narwade, M.L. & Usha, M.S. Studies in adsorption of some toxic metal ions on citrous sinensis skin and Coffea arabica husk: Agricultural by-product. *Asian J. Chem.*, 2002, **14**, 1257.

22. Sanchez Polo, M. & Revera Utrialla. Adsorbent -adsorbate interactions in the adsorption of *Cd*(II) and *Hg*(II) on ozonised activated carbons. *Environ. Sci. Tech.*, 2002, **36**, 3850-854.

23. Gomez-serrane, V.; Macia, A; Garcia, S. & Mansilla, A.E. Adsorption of mercury, cadmium and lead from aqueous solution on heat-treated and sulphurised-activated carbon. *Water Resources*, 1998, **32**, 1.

24. Krishanan, K.A. & Anirudhan, T.S. Removal of mercury (II) from aqueous solutions and chlor-alkali industry effluents by steam-activated and sulphurised-activated carbons prepared by bagasse pith: Kinetics and equilibrium studies. *J Hazardous Materials*, 2002, **92**, 161.

25. Raji, C. & Anirudhan, T.S. Removal of heavy metal ions from water using sawdust-based activated carbon. *Indian J. Chem. Technol.* 1996, (1) 345-51.

26. Siddiqui, A.R.; Sharma P.P. & Sultan, M. Adsorption studies on phosphate-treated sawdust separation of *Cr*(VI) from *Zn*(II), *Ni*(II) and *Cu*(II) and their removal and recovery from electroplating waste. *Ind. J. Environ. Prot.* 1999, **19**(11), 846-52.

27. Nag, N.; Gupta, N.; & Biswas, M.N. Removal of *Cr*(VI) and *Ar*(III) by chemically-treated sawdust. *Ind. J. Environ. Prot.* 1998, **19**(1), 25-29.

28. Yu Bin, *et al.* The removal of heavy metal from aqueous solutions by sawdust adsorption – removal of copper. *J. Hazardous Mater.*, 2000, **80**, 33-42.

29. US Geological Survey, Mineral Commodity Summaries (December, 1997). http://minerals.er.usgs.gov/minerals.

30. APHA, AWWA& WPCF, Standard methods for examination of water and waste water, (19th Edition, American Public Health Association, Washington, DC, USA, 1995.

31. Singh, D. & Rawat, N.S. Adsorption of heavy metals on treated and untreated low grade bituminous coal. *Ind. J. Chem. Tech.*, 1997, **4**, 39-41.

32. Remy, H. Treatise on inorganic chemistry. Elsevie Amsterdam, 1956.

33. Biscarini, P. and Fusinaland Nivellini, G.D. Dissociation and structure of addition compounds between thio-ethers and mercury (II) chloride. *Inorganic chemistry*, 1971, **10**, 2564.

34. Sinha, R.K. & Walker, P.L. Removal of mercury by sulphurised carbon. *Carbon*, 1972, **10**, 754.

35. Valenzuela Calahorro, C. & Macia Garia. Study of sulfur introduction in activated carbon. *Carbon*, 1990, **28**, 321.

Contributors

Mr Ajay Kumar Meena, obtained his MSc (Chemistry) from the University of Rajasthan, Jaipur in 1997. Presently, he is working at the Centre for Fire, Explosive and Environment Safety (CFEES), Delhi. His areas of interest are design and development of treatment technologies for industrial effluents and environmental quality monitoring, and material and process development for environment safety and explosive safety. He has eight papers and several reports to his credit.

Dr G.K. Mishra obtained his PhD(Chemistry) from the Banaras Hindu University, Varanasi in 1992. Presently, he is working as a Scientist at the CFEES, Delhi. His areas of interest are material and process development for environment safety and explosive safety. He has a number of papers and reports to his credit.

Mr Satish Kumar obtained his BSc from the University of Delhi and MA(Public Administration) from the Himachal Pradesh University, in 1999. Presently, he is working as Technical Officer A at the CFEES, Delhi. His areas of interest are design and development of treatment technologies for industrial effluents, contaminated ground water and environmental quality monitoring, and material development for environment safety. He has five papers and several reports to his credit.

Dr (Mrs) Chitra Rajagopal, Chemical Engineer, obtained her PhD from the Indian Institute of Technology (IIT) Delhi, in 1982. Presently, she is working as a Senior Scientist at the CFEES, Delhi. Her areas of interest are hazards and risk analysis, design and development of treatment technologies for industrial effluents and environmental quality monitoring, disaster management, hazardous waste management, and explosive safety. She has also worked on the design of heat transfer systems for specific defence uses. She has more than 50 papers and 25 reports to her credit.

Dr P.N. Nagar, Associate Professor, obtained his MSc and PhD(Chemistry) from the University of Rajasthan, Jaipur. Presently, he is working as a Senior Scientist at the CFEES, Delhi. His areas of interest are synthesis and separation of organo-phosphorous compounds. He has a number of papers and reports to his credit.