Adsorption of Hg(II) from Aqueous Solution of Activated Carbon Impregnated in Copper Chloride Solution

N.T.T. Hai[1,*], N.T. Hue[1] and D.Q. Trung[2]

[1]Institute of Environmental Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Cau Giay District, Hanoi, Vietnam

[2]Hanoi University of Science, Vietnam National University, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam

*Corresponding author: Fax: +84 4 37911203; Tel: +84 912802981; E-mail: nguyenhai2t@gmail.com

Study on removal of mercury in aqueous solution by available and low-cost materials with high treatment efficiency is now-a-day a hot topic. In the present work, activated carbon derived from coconut shell was impregnated with copper chloride solution and removal of Hg(II) from aqueous solution by these carbons was effectively demonstrated. Adsorption of Hg(II) from aqueous solutions was carried out under different experimental conditions by varying solution pH, agitation time, Hg(II) concentration and carbon dosage. It was shown that Hg(II) uptake decreases with increasing pH of the solution and optimum pH value is 6 and equilibrium time was attained at 60, 90 min for activated carbon, copper chloride solution-impregnated activated carbon, respectively. The monolayer adsorption capacity of these particular adsorbents were obtained as 90.9 and 167 mg/g for activated carbon and copper chloride-impregnated activated carbon, respectively. It was determined that Hg(II) adsorption follows both Langmuir and Freundlich isotherms as well as pseudo-first-order kinetics.

Key Words: Activated carbon, Adsorption, Mercury ion, Chloride, Impregnated.

INTRODUCTION

Mercury, as one of the extremely toxic metals and its compounds produce irreversible neurological damage, can be found in wastewaters of some industries, including chlor-alkali, pulp paper, oil refining, electrical, rubber processing and fertilizer industries. Due to its toxic effects, the standard limit of mercury in drinking water is 0.001 mg/g and in industrial wastewater to mix with surface water is 0.01 mg/g[1].

Consequently, removal of mercury ions from water is a very important issue. Treatment methods such as chemical precipitation, coagulation, reverse osmosis, ion exchange, membrane separation[2], have been applied for effective reducing of mercury concentrations from various aqueous solutions. However, most of these methods require either high-energy or large quantities of chemicals. Adsorption, on the other hand, is an effective technique for mercury removal from water. Activated carbons are found to be very effective and among the most extensively used methods for removal of mercury ions. Likewise, activated carbon, as a carbonaceous porous adsorbent, has been investigated for removal of mercury contaminants from water. Low cost and ability to remove the mercury ions are the merits of this carbonaceous adsorbent[3,4].

In recent years, considerable attention has been paid to develop surface-modified adsorbents in order to enhance the adsorption capacity of solids to eliminate mercury from aqueous media. Sulphur[5,6], chloride[7], iodide[8] have been reported as elements which favour the adsorption of mercury. Therefore, the surface treatment which incorporates sulphur or halogenide should improve the entrapment of species that contain mercury.

In the present investigation, the activated carbons derived from coconut shell which is low cost and available in Vietnam was impregnated with copper chloride solution and applied for removal of mercury(II) ion from aqueous solution. The optimum mercury removal conditions such as agitation time, solution pH, Hg(II) concentration and carbon dosage and adsorption kinetics and isotherms were examined.

EXPERIMENTAL

Activated carbon used in this study was produced from coconut shell (Trabac Joint Stock Corporation). The activated carbon was pulverized and sieved to particle diameter of 0.075-0.5 mm. After sieving, the activated carbon was washed with de-ionized water to remove fines, dried in an oven for 24 h at 110 ºC and stored in a desiccator at room temperature until needed.

The impregnated processing was carried out using copper chloride solution 0.3 M (Analytical grade, Merck). 10 g of activated carbon were soaked in 20 mL of copper chloride, at room temperature and shaked on a mechanical shaker (150

rpm) for 5 h. The resulted activated carbon was filtrated with Whatman#1 paper and was washed with de-ionized water several times sequentially to remove any residual chemicals and then dried in an oven at 110 ºC for at least 12 h and placed in a desiccator until needed.

Batch adsorption studies: An adsorbate stock solution of 2000 mg/L Hg(II) was prepared from HgCl₂ (Merck). This solution was diluted to 50-500 mg/L for adsorption experiments.

Two series of experiments were carried out, *i.e.*, a Hg-adsorption kinetics series and a Hg-adsorption isotherms series. The former one was aimed to determine the time necessary to reach the steady state and the Hg(II) removal efficiency by the activated carbons. In this section, optimum contact time, pH range and effects of carbon dosage on the adsorption were examined. The studies were conducted in batch systems at room temperature. For each activated carbon and copper chloride-impregnated activated carbon samples, effects of initial pH solution and contact time on the adsorption carried out by mixing 0.1 g of the carbonaceous samples with 50 mL of 50 mg/L Hg(II) solution while being shaked by a mechanical shaker with agitation speed of 150 rpm, having different initial pH values of 2, 4, 6, 8 and 10 and various contact time of 10, 20, 30, 40, 50, 60, 90, 120 and 150 min were provided. The carbon doses varied from 0.1 to 10 g/L. In all the experiments, after filtration with Whatman#1 papers, the remaining mercury concentration of each solution was determined by atomic absorption spectrophotometer (AA-6800, Shimadzhu, Japan). Method detection limit (MDL) for this instrument is 0.5 µg/L. The Hg(II) concentration retained in the adsorbent was calculated by using eq. (1).

$$q_e = \frac{(C_o - C_e)V}{W}(mg/g) \qquad (1)$$

where C_o and C_e are the initial and equilibrium concentrations of Hg(II) ion in solution, V is the volume of solution and W is the weight of the adsorbent.

The later adsorption series was carried out to draw the adsorption isotherms. In this section, each bottle was filled with 50 mL Hg(II) solution. Hg(II) concentrations varied from 50 to 500 mg/L and the pH was adjusted to 6 using diluted HCl or NaOH solutions. The contact time was 1 h to ensure the equilibration of the adsorption according to the preliminary experiments.

RESULTS AND DISCUSSION

Effect of pH on removal of Hg(II): The pH of the solution plays a vital role in any adsorption process. The pH was adjusted by the addition of HCl and NaOH. It is seen that the removal efficiency of Hg(II) decreases with increasing pH. Some authors indicated that the surface charge is an important factor for the adsorption of metal ions[9,10]. The surface charge is very much dependent on the pH of the solution[11]. By increasing OH⁻ functional group, competing between mercury ions and this group starts and OH⁻ occupies active sites of the adsorbent. Therefore, accessed surface area and subsequently adsorption of mercury ions will be decreased. The effect of pH on mercury adsorption are illustrated in Fig. 1. The maximum

adsorption is observed at pH = 6. In general, the results indicated that adsorption is highly pH-dependent. The adsorption efficiency of Hg(II) has decreased with increasing pH.
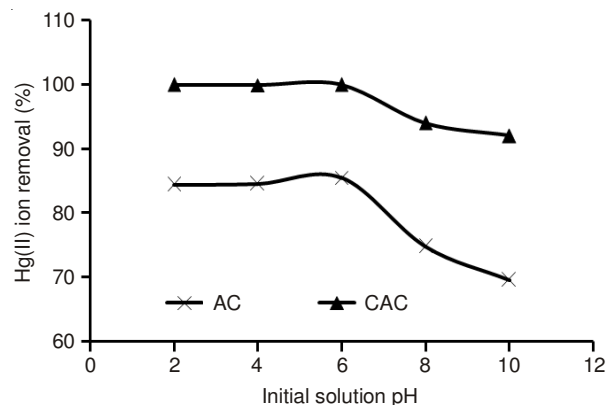

Fig. 1.   Effect of pH on the removal of Hg(II) by activated carbon (AC) and copper chloride-impregnated activated carbon (CAC). Conditions: Hg(II) 50 mg/L; agitation time 1 h; carbon dosage 0.1 g

Effect of agitation time on removal of Hg(II) and adsorption kinetics: Results of the adsorption kinetic experiments are presented in Fig. 2. The adsorption of Hg(II) by the activated carbons increased sharply at a short contact time and slowed down gradually with approaching equilibrium. The times to attain equilibrium were different according to carbon types. Equilibriums were attained at 1 h for activated carbon and 1.5 h for copper chloride-impregnated activated carbon.
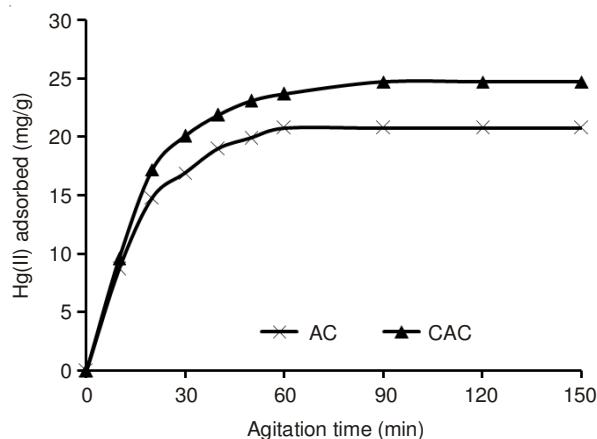

Fig. 2.   Effect of agitation time on the removal of Hg(II) by activated carbon (AC) and copper chloride-impregnated activated carbon (CAC). Conditions: Hg(II) 50 mg/L, initial solution pH 6, carbon dosage 0.1 g

In order to describe the adsorption kinetics for Hg(II) ion on the adsorbent, a first-order rate expression given by Lagergren is applied[12,13]. This model is based on the assumption that chemosorption is the rate limiting step. Model equation is given by:

$$\log(q_e - q) = \log q_e - (K_{ad}/2.303)t \qquad (2)$$

where q is the amount of Hg(II) adsorbed at any time (t) in the unit of mg/g; q_e is the amount of Hg(II) adsorbed at equilibrium (mg/g); K_{ad} is the adsorption rate constant (min⁻¹).

Plotting log (q_e - q) *vs.* t gives straight lines (Fig. 3). The q_e calculated from the plots were 21.9, 24.2 mg/g for activated

	Lagergren		Langmuir				Freundlich		
	K_{ad} (min^{-1})	R^2	K_L (L/mg)	q_{max} (mg/g)	R_L (min-max)	R^2	K_F (mg/g)	n	R^2
Activated carbon	0.062	0.995	0.023	90.9	0.08-0.46	0.994	10.02	2.65	0.971
Copper chloride-impregnated activated carbon	0.053	0.997	0.032	167	0.06-0.39	0.990	14.55	2.19	0.962

TABLE-1
ADSORPTION CONSTANTS FOR Hg(II) UPTAKE BY THE CARBONS

carbon, copper chloride-impregnated activated carbon , respectively. These values have a good agreement with the experimental ones (20.8 and 24.7 mg/g, respectively), indicating that Hg(II) adsorption on the carbons can be approximated to the first order rate expression. The adsorption parameter K_{ad} was calculated from the slope of the plot and was presented in Table-1. K_{ad} values for copper chloride-impregnated activated carbon and activated carbon were within 0.053 and 0.062 min^{-1}, respectively.
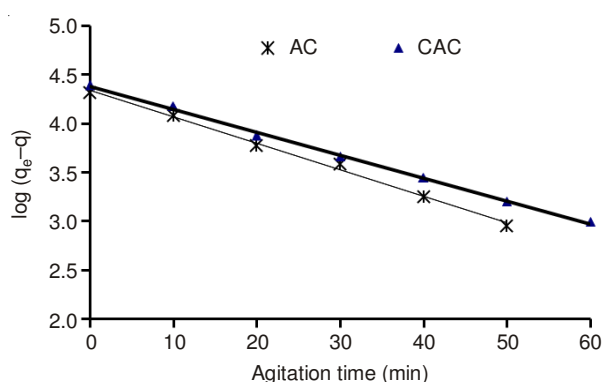

Fig. 3.   Lagergren plots for Hg(II) adsorption onto activated carbon (AC) and copper chloride-impregnated activated carbon (CAC). Conditions: Hg(II) 50 mg/L; initial solution pH 6; carbon dosage 0.1 g

Therefore, among the two types of carbons, although copper chloride-impregnated activated carbon has a higher adsorption capacity for Hg(II), its adsorption rate is relatively lower, thus needs longer time to reach saturation. Furthermore, it is found that the K_{ad} values obtained in this study are consistent with the values obtained from Hg(II) adsorption on activated carbon prepared from agricultural by-product/waste[12] and sulfur-impregnated adsorbent developed from coal[13].

Effect of carbon dosage: Adsorbent dosage is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of Hg(II) ion solution. It was observed that with increasing adsorbent dosage from 0.1 g/L to 10 g/L at a fixed initial Hg(II) concentration of 200 mg/L (Fig. 4). The initial Hg(II) concentration used in this study was relatively higher because according to our preliminary study, a carbon dose of 2 g/L could remove 83-98 % of Hg(II) from an initial concentration of 50 mg/L. Fig. 4 shows in order to remove 200 mg Hg(II) from 1 L aqueous solution, at least 10 g of copper chloride-impregnated activated carbon, but 10 g of activated carbon could only remove 85.7 % of the Hg(II) in the solution.

Adsorption isotherms: The distribution of metal ions between the activated carbon and the metal ion solution for the system at equilibrium is of importance in determining the maximum adsorption capacity of the activated carbon. The
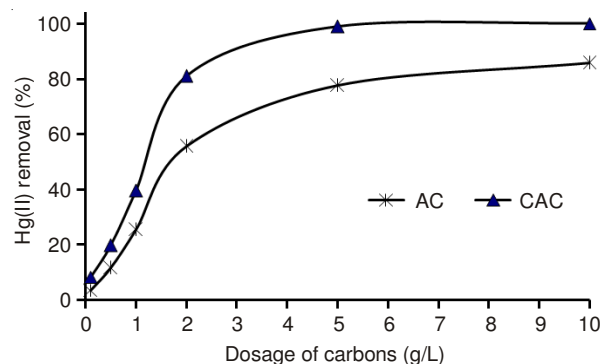

Fig. 4.   Effect of carbon dosage on removal of Hg(II) from aqueous solution. Conditions: Hg(II) 200 mg/L; initial solution pH 6

experimental data relating to the adsorption of Hg(II) onto activated carbon and copper chloride-impregnated activated carbon adsorbents are interpreted by Langmuir[14] and Freundlich[15] adsorption isotherm models and the isotherms are graphically shown in Figs. 5 and 6. The linear forms of Langmuir and Freundlich models are represented by eqs. 3 and 4:

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{1}{Q_o}C_e \tag{3}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{4}$$

where C_e is the equilibrium concentration of the solute (mg/L); q_e is the maximum amount (mg) of solute adsorbed per gram, K_F, n, Q_o and b are characteristic constants.

The value of K_F has been used as a relative measure of adsorption capacity, n, Q_o and b are related to enthalpy and intensity of adsorption. Figs. 5 and 6 show the applicability of both models over a wide range of concentrations. Freundlich and Langmuir parameters are given in Table-1.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L[16] which is defined by:
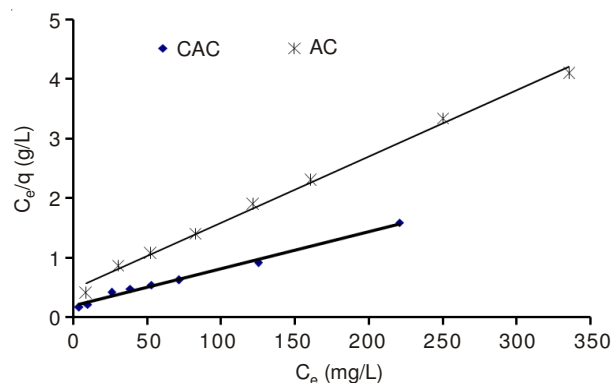

Fig. 5.   Langmuir isotherms for adsorption of Hg(II) ions from aqueous solution. Conditions: dosage of carbon 0.1 g; initial solution pH 6
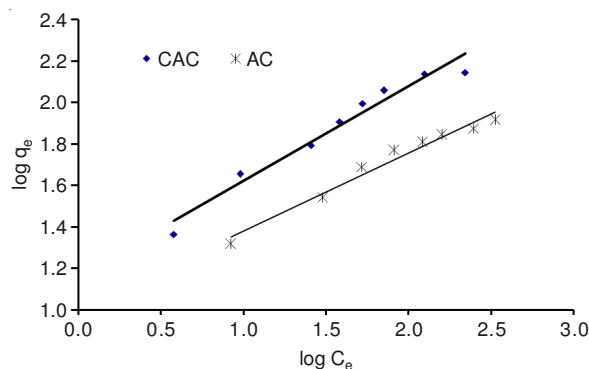
Fig. 6. Freundlich isotherms for adsorption of Hg(II) ions from aqueous solution. Conditions: dosage of carbon 0.1 g; initial solution pH 6

$$R_L = 1/(1 + bC_o) \qquad (5)$$

where b is Langmuir constant and C_o is the initial concentration of metal ions. According to Hall *et al.*[16], the parameter R_L indicates the shape of the isotherm as follows: R_L value type of isotherm ($R_L > 1$ unfavourable; $R_L = 1$ linear; $0 < R_L < 1$ favourable; $R_L = 0$ irreversible).

The R_L values between 0 and 1 show that the adsorption is favourable (Table-1). The adsorption capacities of copper chloride-impregnated activated carbon are higher than activated carbon (Table-1).

Freundlich coefficient, K_F, which represents the adsorption capacity, was 10.02 for activated carbon, 14.55 for copper chloride-impregnated activated carbon. The other Freundlich coefficient 'n' values were 2.65 for activated carbon, 2.19 for copper chloride-impregnated activated carbon fulfilling the condition of $1 < n < 10$ for favourable adsorption. The correlation coefficients showed that in general, the Langmuir model fitted the results slightly better than the Freundlich model.

Conclusion

Activated carbon derived from coconut shell was impregnated with copper chloride and removal of Hg(II) from aqueous solution by these carbons was effectively demonstrated.

The optimum conditions for the removal of mercury is at pH 6, contact time 1 h for activated carbon; pH 6, contact time 1.5 h for copper chloride-impregnated activated carbon. The

monolayer adsorption capacity of these particular adsorbents were obtained as 90.9 and 167 mg/g for activated carbon and copper chloride-impregnated activated carbon, respectively. Higher removal of mercury by copper chloride-impregnated activated carbon may be due to presence of chloride functional group and the adsorption capacities increased along with the increase of Hg(II) concentration. 10 g of copper chloride solution was sufficient for removal of 200 mg Hg(II) from 1 L aqueous solution, but 10 g of activated carbon could only remove 85.7 % of the Hg(II) in the solution. In the present paper, it is shown that the copper chloride-impregnated activated carbon is useful for effective and economical treatment of wastewater containing mercury metal ions. Both the Freundlich and Langmuir models could be used to fit the data and estimate model parameters. The fit was slightly better for the Langmuir model.

REFERENCES

1. ISI, Tolerance Limits for Industrial Effluents Prescribed by Indian Standards Institution IS: 2490 (1981).
2. M. Kobya, E. Demirbas, E. Senturk and M. Ince, *Bioresour. Technol.*, **96**, 1518 (2005).
3. J. Goel, K. Kadirvelu, C. Rajagopal and V. Garg, *Carbon*, **43**, 197 (2005).
4. M. Yardim, T. Budinova, E. Ekinci, N. Petrov, M. Razvigorova and V. Minkova, *Chemosphere*, **52**, 835 (2003).
5. D. Karatza and A. Lancia, *Exp. Thermal Fluid Sci.*, **21**, 150 (2000).
6. H. Hsi, M.J. Rood and M.R. Abadi, *J. Environ. Eng.*, **128**, 1080 (2002).
7. H. Zeng, F. Jin and J. Guo, *Fuel*, **83**, 143 (2004).
8. S.J. Lee, Y.C. Seo, J.S. Jurng and T.G. Lee, *Atmos. Environ.*, **38**, 4887 (2004).
9. W.R. Knocke and L.H. Hemphill, *Water Res.*, **15**, 275 (1981).
10. M.K. Sreedhar, A. Madhukumar and T.S. Anirudhan, *Indian J. Eng. Mater. Sci*, **6**, 279 (1999).
11. C.P. Huang, Chemical Interactions Between Inorganic and Activated Carbon, Carbon Adsorption Handbook, Ann Arbor Science, Ann Arbor, MI, pp. 281-329 (1978).
12. M.M. Rao, D.H.K.K. Reddy, P. Venkateswarlu and K. Seshaiah, *J. Environ. Manag.*, **90**, 634 (2009).
13. T. Wajima and K. Sugawara, *Fuel Proc. Technol.*, **92**, 1322 (2011).
14. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
15. H.M.F. Freundlich, *Z. Phys. Chem.*, **57**, 384 (1906).
16. K.R. Hall, L.C. Eagleton, A. Acrivos and T. Vermeulen, *Ind. Eng. Chem. Fundam.*, **5**, 212 (1966).