Adsorption of Functionalized Thiol-Graphene Oxide for Removal of Mercury from Aqueous Solution†

Prawit Nuengmatcha, Ratana Mahachai and Saksit Chanthai[*]

Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

*Corresponding author: E-mail: sakcha2@kku.ac.th

Graphene oxide (GO) was optimally produced from graphite as a starting material and was subject to functionalize with 3-mercaptopropyl-trimethoxysilane to acquire thiol group (-SH) as a selective carbon-based adsorbent for the removal of mercury from aqueous solution comparing with its bare graphite. The GO-SH was characterized by Fourier transform infrared spectroscopy and energy dispersive X-ray spectroscopy. IR characteristic peaks appear at wave numbers of 3367 ν(O-H), 2576 ν(S-H), 1719 ν(C=O), 1224 and 1049 ν(C-O) and 1160 ν(Si-O-C) indicating the thiol group attached. Also, EDX spectrum revealing both Si and S peaks confirms the 3-mercaptopropyl-trimethoxysilane bound on the graphene oxide surface. For an optimal adsorption study, the effects of pH solution, contact time and initial concentration of Hg(II) were investigated in association with determination of Hg(II) by HGAAS. From the results, the adsorption capacity of the functionalized GO-SH for Hg(II) was 80.65 mg/g at pH 6.6, about 3 times higher than that of its bare graphite (22.94 mg/g). The adsorption isotherm of the GO-SH for Hg(II) was found only fitting well with Langmuir model, while that of bare graphite followed the Freundlich one. It is implied that graphene oxide modified with thiol can be used as a high potential adsorbent for such toxic metals.

Keywords: Graphene oxide, Mercury, 3-Mercaptopropyl-trimethoxysilane.

INTRODUCTION

Mercury is one of highly toxic and accumulative metals. Mercury and its compounds are neurotoxins which cause blockage of the enzyme sites and interfere in protein syntheses[1]. Thus, it is necessary to remove these metal contaminants from the wastewater before releasing into the environment to protect both environment and human being. Adsorption technique is the most promising process for the removal of metal ions from wastewater. Although several carbon-based adsorbents for metal removal using adsorption technique[2-5], graphene oxide (GO) is an alternative choice of the carbon-based adsorbents. The abundance of the functional groups on the graphene oxide surface can be modified with several ligands, making it a potential material as a super adsorbent. Particularly, the mercapto or thiol group (-SH group) has a high ability to adsorb toxic metal ions, this unique characteristic reveals that the thiol group has potential applications in the removal of toxic metal ions from wastewater[6-9].

In this study, the prepared graphene oxide was modified with 3-mercaptopropyl-trimethoxysilane (MPTMS) to acquire the functionalized GO-SH and then applied to remove Hg(II) from aqueous solution. An evaluation of the potential use of the GO-SH for Hg(II) in a batch adsorption study was compared with its bare graphite (BGP). The effects of pH solution, contact time and an initial concentration of Hg(II) were optimized. Both Langmuir and Freundlich isotherms were also investigated to fit their adsorption model for Hg(II) removal.

EXPERIMENTAL

Preparation and characterization of graphene oxide and GO-SH: Graphene oxide was prepared from graphite powder by the modified Hummers' method[10]. In brief, 3 g of graphite powder was added to cold (about 0 °C) 300 mL of 98 % H_2SO_4 and stirred for 0.5 h. Then, 3.0 g of $NaNO_3$ was added portion-wise to the mixture and kept further stirring for 0.5 h. Subsequently, a solid powder of $KMnO_4$ (4.5 %, w/v) was added to the mixture, which always kept below 10 °C in an ice bath. After stirring for 0.5 h, 200 mL of deionized water was then slowly added to the mixture and stirred again for 0.5 h. After heating up to 80 °C for 6 h, 40 mL of 30 % H_2O_2 was slowly added. The solution mixture was centrifuged and washed several times with deionized water until the pH of the filtrate reached neutral. Then, the lyophilized precipitates were obtained.

To functionalized graphene oxide with MPTMS, 200 mg of graphene oxide was added to round flask with 25 mL ethanol and dispersed through ultra-sonication for 0.5 h. Then 4.8 % w/v of MPTMS was added and ultra-sonicated next for 0.5 h. After that the mixture stirred at 65 °C for 12 h. The GO-SH product was centrifuged and washed with ethanol and oven-dried at 50 °C for 12 h. The obtained GO-SH was characterized by FTIR and EDX techniques.

Adsorption experiment: For a batch adsorption of Hg(II), adsorbent (0.02 g) was accurately weighed into a 125 mL conical flask. Then, 25 mL of Hg(II) solution (various concentrations) was added and the pH of the solution was adjusted and shaken by an orbital shaker at approximately 200 rpm at ambient temperature (30 °C). For optimum conditions, various experimental parameters including pH solution (pH 2-9), contact time (10-100 min) and an initial concentration of Hg(II) (0.1-60 mg/L) were investigated. After a period of shaking, the adsorbent was separated from the solution mixture by centrifugation for 5 min and Hg(II) in the supernatant solution was determined by FI-HGAAS. All experiments were conducted in triplicate under the same conditions. The adsorption capacity (q_e, mg/g) of mercury at an equilibrium state was determined as follows:

$$q_e = \frac{V(C_o - C_e)}{m} \tag{1}$$

where C_o is the initial concentration (mg/L) of Hg(II) in the solution, C_e is the Hg(II) concentration (mg/L) at the equilibrium state, V is the volume (L) of the solution and m is the mass (g) of the adsorbent. Langmuir and Freundlich adsorption models were used to describe the equilibrium nature of mercury adsorption onto the GO-SH compared with bare graphite adsorbent as a background reference.

RESULTS AND DISCUSSION

Characterization of adsorbents: To confirm the existence of MPTMS on graphene oxide, FTIR and EDX spectroscopy were performed. From the spectra in Fig. 1(a), it is evident that the changes in the adsorption peaks of MPTMS, GO-SH and graphene oxide are differently found. The peak at 3367 cm^{-1} was the stretching of -OH groups. The C-H stretching of CH$_3$ and CH$_2$ groups appeared at 2925 cm^{-1} and 2864 cm^{-1}, respectively. The band at 1160 cm^{-1} was the stretching vibration

of Si-O-C confirming the formation of GO-SH. Moreover, it is noted that the stretching vibration of -SH group[6] occurred at 2576 cm^{-1} which proved the existence of the functionalized -SH groups on the graphene oxide surface. Furthermore, from EDX patterns in Fig. 1(b), it is shown that the changes in the spectra of MPTMS, GO-SH and graphene oxide are obviously different. The peak of Si and S were occurred only in GO-SH; indicating that graphene oxide modified with thiol was successfully obtained. This observation suggests that graphene oxide really contain -SH group, which can be applied to selectively remove Hg(II) from aqueous solution.

Adsorption experiment: The influence of an initial pH on the adsorption efficiency was evaluated in terms of adsorption capacity. Fig. 2(a) shows the adsorption capacity and removal percentage of Hg(II) at different pH values in the range of 2-9. It was found that the adsorptions of Hg(II) increased with the pH of the solution. The maximum adsorption capacity was taken place at pH 6.6 (5.70 mg/g). The pH value at the point of zero charge (pH$_{PZC}$) of GO-SH has been reported to be 5.1. At higher pH, surface of the adsorbent had got negatively charged and favoured uptake of Hg(II). Therefore, the maximum adsorption capacity of GO-SH was occurred at pH higher than 6.6.

The effect of contact time on Hg(II) adsorption onto the GO-SH adsorbent. From Fig. 2(b), it is clearly shown that the rate of adsorption and removal percentage increased at an initial period of a contact time and it decreased gradually with time until the adsorption reached an equilibrium point. The equilibrium time was established within 1 h. Therefore, further studies were carried out at a period of 1 h as a suitable contact time for Hg(II) adsorption on the GO-SH.

The effect of an initial concentration of Hg(II) is considered to be an important one because it can overcome all mass transfer restrictions of Hg(II) between the aqueous phase and the solid phase. From the result shows that the equilibrium adsorption capacity increased with increasing an initial concentration indicating that higher initial concentration of Hg(II) can enhance the adsorption process. The maximum value of the equilibrium adsorption capacity at 20 mg/L Hg(II) concentration for GO-SH was found to be 69.52 mg/g. Increase in the uptake capacity of GO-SH adsorbent with increasing of an initial Hg(II) concentration may be due to the higher collision probability between Hg(II) ions and the adsorbent particles.
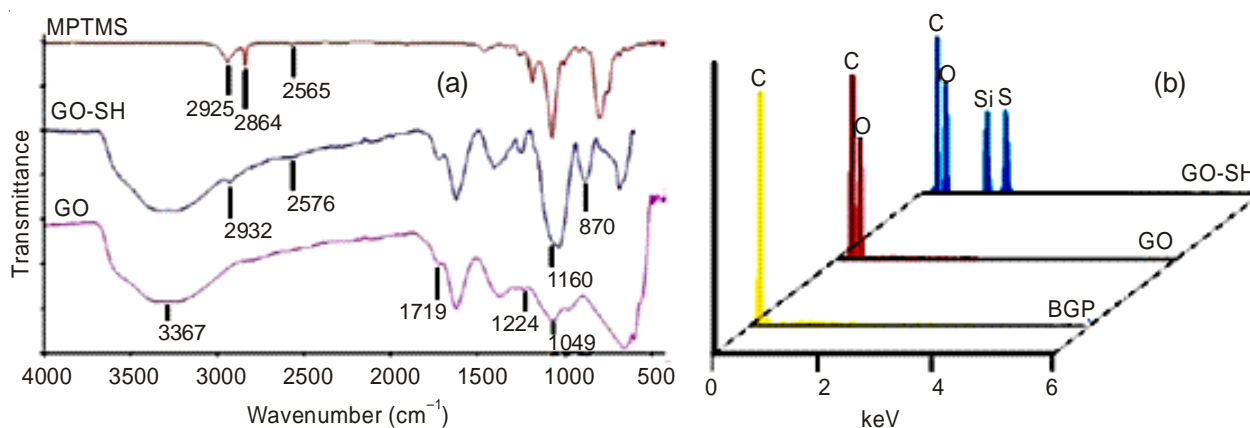

Fig. 1. (a) FTIR spectra of MPTMS, GO-SH and graphene oxide and (b) EDX patterns of bare graphite, graphene oxide and GO-SH
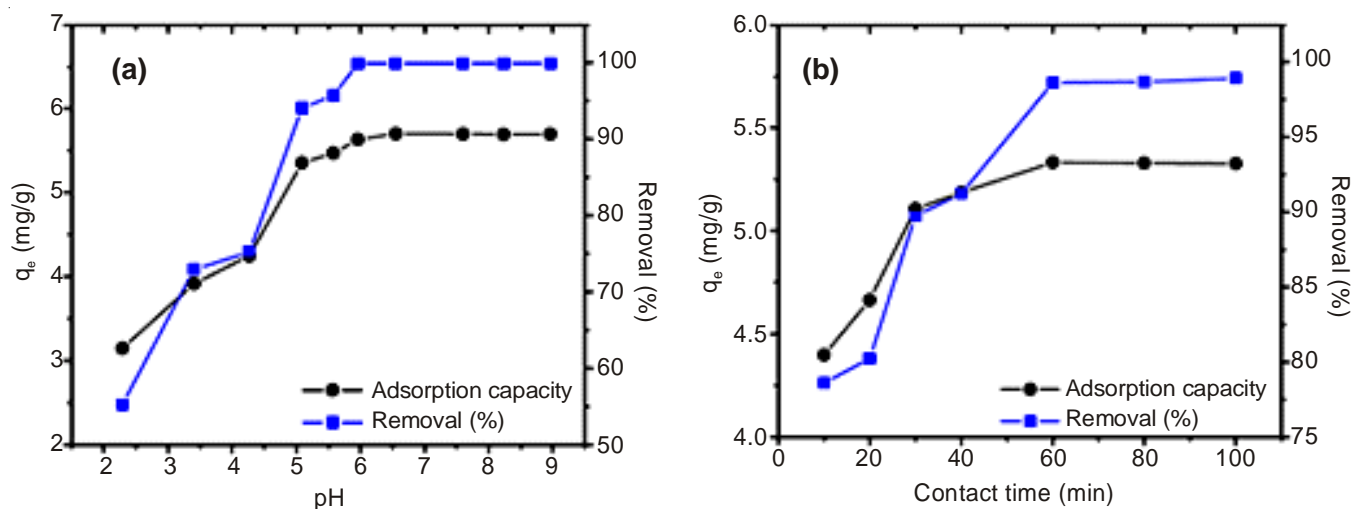
Fig. 2. Effects of pH (a) and contact time (b) on adsorption of Hg(II) using GO-SH adsorbent

Adsorption isotherm: Langmuir and Freundlich models are the most frequently used to describe the adsorption isotherms. For the Langmuir model, the adsorption takes place only at specific sites of the adsorbent, which is valid for monolayer sorption onto a surface, given by

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (2)$$

where q_m is the maximum amount of the Hg(II) absorbed per unit weight of adsorbent (mg/g) to form a complete monolayer covered on the surface at equilibrium Hg(II) concentration, C_e (mg/L), q_e is the amount of Hg(II) adsorbed per unit weight of adsorbent at equilibrium and K_L is the Langmuir constant (L/mg). The values of q_m and K_L are calculated from the slopes and the intercepts of the straight line of the plots of C_e/q_e versus C_e.

The Freundlich adsorption isotherm is the equation to describe the heterogeneous surface. The mathematical form of Freundlich adsorption isotherm is represented by eqn. 3.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where, K_F and n are the Freundlich constants and an intensity of adsorption, respectively. Both values of K_F and 1/n (between 0 and 1) can be obtained from the linear plots of log q_e versus log C_e. The constant values obtained from both Langmuir and Freundlich adsorption isotherms and their correlation coefficients (R^2) were calculated and are summarized in Table-1. From the results, it can be concluded that for bare graphite adsorbent, the Freundlich isotherm ($R^2 > 0.99$) fitted the experimental results better than the Langmuir isotherm ($R^2 > 0.89$). The slope 1/n provides information about surface heterogeneity and surface affinity for the solute. If a higher value of 1/n is obtained, it corresponds to the greater heterogeneity of the adsorbent surface. On the other hand, for GO-SH adsorbent, the Langmuir isotherm ($R^2 > 0.99$) fitted the experimental results better than the Freundlich isotherm ($R^2 > 0.85$). It corresponds to the homogenous adsorbent surface. The Hg(II) ions were taken place only at specific sites of the GO-SH adsorbent, which is valid for monolayer sorption onto

TABLE-1
LANGMUIR AND FREUNDLICH
ISOTHERMS FOR Hg(II) ADSORPTION

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	K_L	R^2	K_F	1/n	R^2
GO-SH	80.65	2.00	0.9999	57.65	0.09	0.8580
BGP	22.94	0.06	0.8958	2.19	0.49	0.9977

a surface. The maximum values of adsorption capacity were 22.94 and 80.65 mg/g for bare graphite and GO-SH, respectively. For comparison, the maximum adsorption capacities of Hg(II) using several other adsorbents are presented in Table-2. It is evident that GO-SH possesses high adsorption capacity for Hg(II) removal from the aqueous solution compared with the other carbon-based adsorbents.

TABLE-2
ADSORPTION CAPACITY OF Hg(II) USING
VARIOUS CARBON-BASED ADSORBENTS

Adsorbent	q_m (mg/g)	Ref.
Carbon aerogel	45.62	11
Sulfur-impregnated activated carbon	43-72	12
Coal adsorbent (*Bolluca*)	37	13
Activated carbon prepared from *C. pentandra* hull	25.88	14
Functionalized thiol-graphene oxide	80.65	This work
Commercial graphite	22.94	This work

Conclusion

The present study reveals the feasibility of using functionalized graphene oxide with 3-mercaptopropyl-trimethoxysilane for the removal of Hg(II) from aqueous solution. FTIR and EDX techniques were performed to successfully confirm the 3-mercaptopropyl-trimethoxysilane bound on the surface of graphene oxide. Their adsorption behaviours are well described by Langmuir and Freundlich isotherm models. The maximum adsorption capacity of GO-SH for Hg(II) was 80.65 mg/g, about 3 times higher than that of its bare graphite (22.94 mg/g) according to their relevant functional groups.

REFERENCES

1. M. Hadavifar, N. Bahramifar, H. Younesi and Q. Li, *Chem. Eng. J.*, **237**, 217 (2014).
2. C. Xiong, Q. Jia, X. Chen, G. Wang and C. Yao, *Ind. Eng. Chem. Res.*, **52**, 4978 (2013).
3. R. Wahi, Z. Ngaini and V.U. Jok, *World Appl. Sci. J.*, **5 (special issue)**, 84 (2009).
4. F.S. Zhang, J.O. Nriagu and H. Itoh, *Water Res.*, **39**, 389 (2005).
5. X. Lu, J. Jiang, K. Sun, J. Wang and Y. Zhang, *Mar. Pollut. Bull.*, **78**, 69 (2014).
6. Y. Zhang, X. Wang, J. Liu and L. Wu, *J. Chem. Data*, **58**, 1141 (2013).
7. Y. Park, H. Lee, S.B. Park, M.-H. Oh, K. Cho, S. Suzuki, M. Nagai and F.B. Prinz, *J. Korean Phys. Soc.*, **56**, 1215 (2010).
8. K.H. Nam, S. Gomez-Salazar and L.L. Tavlarides, *Ind. Eng. Chem. Res.*, **42**, 1955 (2003).
9. J.M. Arsuaga, J. Aguado, A. Arencibia and M.S. López-Gutiérrez, *Adsorption*, **20**, 311 (2014).
10. W.S. Hummers Jr. and R.E. Offeman, *J. Am. Chem. Soc.*, **80**, 1339 (1958).
11. A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal and P.N. Nagar, *J. Hazard. Mater.*, **122**, 161 (2005).
12. J.H. Cai and C.Q. Jia, *Ind. Eng. Chem. Res.*, **49**, 2716 (2010).
13. E. Ekinci, T. Budinova, F. Yardim, N. Petrov, M. Razvigorova and V. Minkova, *Fuel Process. Technol.*, **77-78**, 437 (2002).
14. M.M. Rao, D.H.K.K. Reddy, P. Venkateswarlu and K. Seshaiah, *J. Environ. Manage.*, **90**, 634 (2009).