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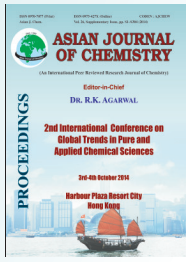

Removal of Hg(II) from Aqueous Solution Using Graphene Oxide as Highly Potential Adsorbent

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Mercury and its compounds are neurotoxins, which simply cause any blockage of enzyme sites and interfere in related protein synthesis and generally found as much toxic metal contaminants in wastewater and environment. Removal of such metal ions by various adsorbents including chitosan, resins, ash, silica gel and activated carbon was reported. Presently, graphene oxide is one of the highly potential adsorbents used in numerous applications. Its main advantage consists of three main functional groups (carbonyl, hydroxyl and epoxide) on their surface giving anchored sites for metal ions complexation, namely for adsorption capabilities of Pb(II), Zn(II), Cu(II), Cd(II) and Co(II). The present study was thus subject to the adsorption of Hg(II) with graphene oxide compared with bare graphite. For an optimization study, the effects of pH solution (2-9), incubation time (10-240 min) and an initial concentration of Hg(II) (0.1-60 mg/L) were investigated. Mercury(II) ion was analyzed by FI-HGAAS. From the results, the adsorption capacity for Hg(II) removal from aqueous solution was 50.51 mg/g at pH 4.4 and their adsorption state was completed within 80 min. While bare graphite gave the adsorption capacity of 22.94 mg Hg(II)/g at pH 6.5 within 100 min. The adsorption isotherms of Hg(II) fit well with the Langmuir and Freundlich models for graphene oxide and bare graphite, respectively. It is demonstrated that graphene oxide can also be a highly potential adsorbent for toxic metals.

Keywords: Graphene oxide, Mercury(II), Adsorption capacity, FI-HGAAS.

INTRODUCTION

Some of toxic metals such as lead, cadmium, chromium and mercury contaminating in an environment are mainly released from industrial activities, for example; metallurgical and chemical manufacturing, automobile and battery factory and mining process[1-3]. When disposing of those toxic metals into the environments, they are bio-accumulated in an aquatic life[4-6]. Particularly a highly toxic and accumulative metal, mercury and its compounds are neurotoxins which cause blockage of the enzyme sites and interfere in protein syntheses. Moreover, the fate of inorganic mercury ion in nature is turning it into methyl mercury due to the aerobic action of microorganism[7] resulted in the food chain contaminated and further getting risk of human hazard. Thus, it is necessary to remove these metal contaminants from the wastewater before releasing into the environment to protect both environment and human being.

In the present, there are many removal methods of Hg(II) from wastewater such as coprecipitation, electrocoagulation, reduction reaction, membrane filtration, reverse osmosis, ion exchange, adsorption and other techniques[8-11]. Among these techniques, adsorption is the most promising process for the removal of metal ions from wastewater. Adsorption technique is basically relied on interactions between adsorbent and adsorbate. Several carbon-based adsorbents for metal removal include chitosan[12], longan shell[13], soybean stalk[14], resins[15], bamboo leaf powder[16], rice straw[17], rice husk ash[18], silica gel[19] and activated carbon[20-22]. However, disadvantages of these natural adsorbents are either low efficiency or low adsorption capacity, thus new adsorbents have been developed to maximize their adsorption property with higher capacity and selectivity.

Recently, graphene oxide is an alternative choice of the carbon-based adsorbents. It is an ideal adsorbent for wastewater treatment because of non-specific functional groups (carbonyl, hydroxyl and epoxide) on their surface providing anchor sites for metal ion complexation[2]. The abundance of the functional groups on the graphene oxide surface exhibits a capability of graphene oxide for metal adsorption such as Pb(II)[2], Zn(II)[23], Cu(II)[24], As(V)[25], Cd(II)[26], Cr(VI)[27] and Co(II)[28].

In this study, graphene oxide was prepared from commercial graphite and applied to remove Hg(II) from aqueous solution. An evaluation of the potential use of the graphene oxide for Hg(II) in a batch adsorption study was compared

with its bare graphite. The effects of pH solution, incubation time and an initial concentration of Hg(II) were optimized. Langmuirand Freundlich isotherms were also investigated in detail to fit an adsorption model for Hg(II) removal from aqueous solution.

EXPERIMENTAL

Sodium nitrate, sulfuric acid (98 %, w/v) and hydrogen peroxide (30 %, v/v) were purchased from Ajax Fine Chem Pty Ltd. Potassium permanganate and synthetic graphite power (< 20 μm) were purchased from Carlo Erba and Sigma-Aldrich, respectively. Hg(II) ion was determined using flow injection-hydride generation equipped with quartz tube furnace atomic absorption spectrometry (FI-HGQTFAAS).

Preparation of graphene oxide: Graphene oxide was prepared from graphite powder by the modified Hummers' method[29]. In a typical synthesis, 3 g of graphite powder was added to cold (about 0 °C) 300 mL of 98 % H_2SO_4 and stirred for 30 min. Then, 3 g of $NaNO_3$ was added portion-wise to the mixture and kept further stirring for 30 min. 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 de-ionized 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 de-ionized water until the pH of the filtrate reached neutral. Then, the lyophilized precipitates were obtained

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 (20 mg/L) was added and the pH of the solution was adjusted and shaken by an orbital shakerat approximately 200 rpm at ambient temperature (30 ºC). For optimum conditions, various experimental parameters including pH solution (2-9), incubation time (10-240 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 byFI-HGQTFAAS. 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:

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

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 graphene oxide compared with bare graphite adsorbent.

RESULTS AND DISCUSSION

Effect of pH: The pH of aqueous solution is a very critical parameter affecting the adsorption process due to functional groups of both adsorbed molecules and adsorbent particles being affected by the concentration of hydrogen ions (H^+) in the solution. The H^+ in solution are involved in the adsorption process at the active sites of the adsorbent. The influence of initial pH on the adsorption efficiency was evaluated in terms of adsorption capacity. Fig. 1 shows the adsorption capacity of Hg(II) at different pH values in the range of 2-9. It was observed that the adsorptions of Hg(II) increased with the pH of the solution. At pH 2, the extent of Hg(II) adsorptionwas nearly the same (1.5 and 1.6 mg/g for bare graphite and graphene oxide, respectively). The adsorption capacity increases up to pH about 5 and there after the change of adsorption capacity was kept constant. The maximum adsorption capacities were taken place at pH 4.4 and 6.6 for graphene oxide (2.6 mg/g) and bare graphite (1.8 mg/g), respectively. The pH values at the point of zero charge (pH_{PZC}) of graphene oxide and bare graphite have been previously reported to be 4.1 and 6.5, respectively. At lower pH, the adsorption capacities of graphene oxide and bare graphite were lower due to the competition between H^+ and Hg^{2+} ions for their adsorption sites causing in decrease of the adsorption. In addition, at acidic solution, the adsorbent surface becomes positively charged and not favored uptake of Hg(II). On the other hand, at higher pH, the surface of adsorbents got negatively charged and favored uptake of Hg(II). Therefore, the maximum adsorption capacity of graphene oxide and bare graphite were occurred at pH higher than 4.1 and 6.5, respectively.

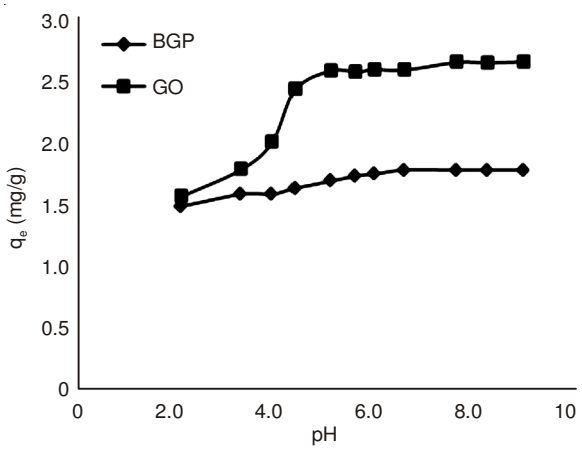

Fig. 1. Effect of pH solution on adsorption of Hg(II) using graphene oxide and bare graphite as adsorbents

Effect of incubation time: The effect of incubation time on Hg(II) adsorption onto the graphene oxide and bare graphite adsorbents at 20 mg/L of the initial Hg(II) concentration at pH 4.4 and 6.6, respectively, was evaluated. Fig. 2 showed that the rate of adsorption increased at an initial period of an incubation time and it decreased gradually with time until the adsorption reached an equilibrium point. The equilibrium time was established within 80 and 100 min for graphene oxide and bare graphite, respectively. At the initial stage (first 50 min), the Hg(II) adsorption rate may be explained by an increased availability in the number of active sites on the surface of both adsorbents. The adsorption amount of Hg(II) on adsorbent drastically increased and normally controlled by the diffusion process from the bulk to the surface of adsorbent. In the final stage, the adsorption amount of Hg(II) was likely an attachment

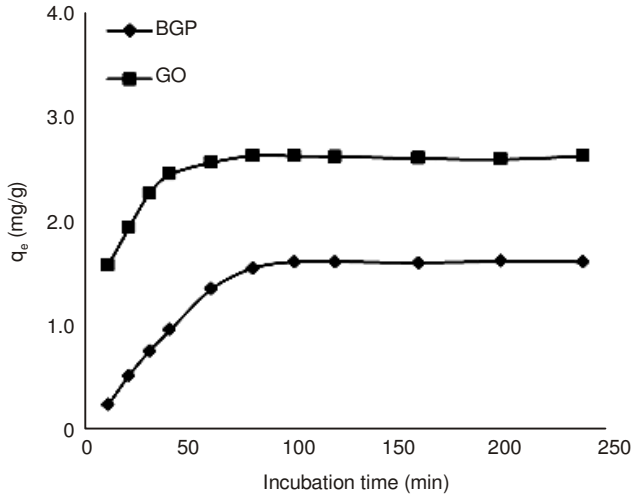

Fig. 2. Effect of incubation time on adsorption of Hg(II) using graphene oxide and bare graphite as adsorbents

controlled process due to less available sorption sites[16]. Therefore, further studies were carried out at a period of 80 and 100 min as a suitable incubation time for Hg(II) adsorption on graphene oxide and bare graphite sorbents, respectively.

Effect of an initial concentration of Hg(II): The effect of an initial concentration of Hg(II) is considered to be important one because it can overcome all mass transfer restrictions of Hg(II) between the aqueous phase and the solid phase. Fig. 3 shows plots of equilibrium adsorption capacity *versus* the initial concentration of Hg(II) on graphene oxide and bare graphite adsorbents. It is clear 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 values of the equilibrium adsorption capacity at 20 mg/L Hg(II) concentration for graphene oxide and bare graphite were found to be 39.5 and 14.3 mg/g, respectively. Increase in the uptake capacity of graphene oxide and bare graphite adsorbents with increasing of an initial Hg(II) concentration may be due to the higher collision probability between Hg(II) ions and the adsorbent particles. Moreover, variation in the extent of adsorption may also be due to the fact that initial all active sites on the surface of the adsorbent were vacant and the concentration gradient of Hg(II) was relatively high.

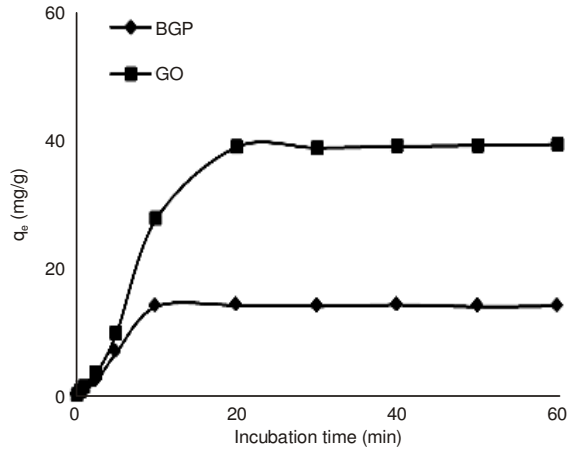

Fig. 3. Effect of an initial concentration of Hg(II) on adsorption capacity using graphene oxide and bare graphite as adsorbents

Adsorption isotherm: The interaction between liquid phase and adsorbent is described by the adsorption isotherms. These mathematical descriptions of the equilibrium adsorption capacity in the adsorption process provide a reliable prediction of the adsorption parameters and quantitative comparison to the adsorption behaviours for different adsorbent systems. The Langmuir model assumes that a monolayer of adsorbate is covered on a homogenous adsorbent surface. 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) related to the surface affinity for Hg(II). The value of q_m represents a practical limiting adsorption capacity when the surface is fully covered with Hg(II) ions. 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 *vs*. C_e.

The Freundlich adsorption isotherm is the equation to describe the heterogeneous surface. The mathematical form of Freundlich adsorption isothermis 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. Figs. 4 and 5 show the fitting plots of Langmuir adsorption and Freundlich adsorption of Hg(II) onto graphene oxide and bare graphite, respectively. 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 graphene oxide adsorbent, the Langmuir isotherm ($R^2 > 0.99$) fitted the experimental results better than the Freundlich isotherm ($R^2 > 0.93$). It corresponds to the homogenous adsorbent surface. The Hg(II) ions were taken place only at specific sites of the graphene oxide adsorbent, which is valid for monolayer sorption onto a surface. The maximum values of adsorption capacity were 22.94 and 50.51 mg/g for bare graphite and graphene oxide, respectively. For comparison, the maximum adsorption capacity of Hg(II) using several other adsorbents are presented in Table-2. It is evident that graphene oxide possess high adsorption capacity for Hg(II) removal from the aqueous solution compared with the other carbon-based adsorbents.

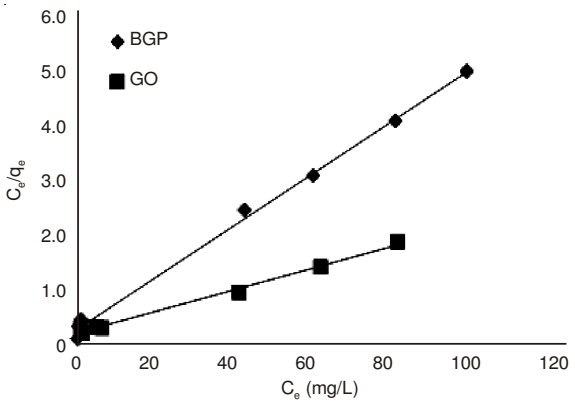

Fig. 4. Langmuir plot of Hg(II) using graphene oxide and bare graphite as adsorbents

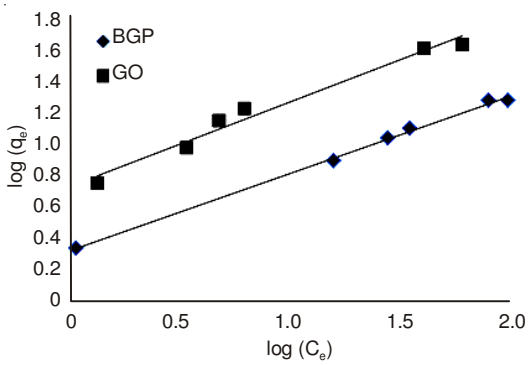

Fig. 5. Freundlich plot of Hg(II) using graphene oxide and bare graphite as adsorbents

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

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	$q_{max\ (mg/g)}$	K_L	R^2	K_F	1/n	R^2
Graphene oxide	22.94	0.057	0.8958	2.19	0.4907	0.9977
Bare graphite	50.51	0.089	0.9934	5.76	0.4995	0.9389

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

Adsorbent	q_m(mg/g)	Ref.
Bamboo leaf powder	27.11	16
Activated carbon of palm oil empty fruit bunch	52.67	20
Carbon aerogel	45.62	30
Sulfur-impregnated activated carbons (SIACs)	43.72	31
Commercial SIAC	41.00	31
Coal adsorbents (*Bolluca*)	37.00	32
Activated carbon prepared from *C. pentandra*hulls	25.88	33
Activated carbon prepared from *P. aureus* hulls	23.66	33
Activated carbon prepared from *C. arietinum*waste	22.88	33
Graphene oxide	50.51	This work
Commercial graphite	22.94	This work

Conclusion

The present study reveals the feasibility of using graphene oxide derived from a synthetic graphite powder for the removal of Hg(II) from aqueous solution. Their adsorption behavior is well described by Langmuir and Freundlich isotherm models. The maximum adsorption capacity of graphene oxidefor Hg(II) was 50.51 mg/g, about twice times higher than that of its bare graphite (22.94 mg/g) according to their relevant functional groups.

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