Kinetics and Thermodynamics of Hg(II) Adsorption on Modified Vermiculite

XIANG-JING AN, YU QI, HONG-LING LI and JIAN-MING DAN[*]

School of Chemistry and Chemical Engineering, Key Laboratory for Green Process of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, Xinjiang Province, P.R. China

*Corresponding author: Tel: +86 13319932155; Email: axjshzdx@gmail.com; 548606252@qq.com

This study investigated the processing of mercury-bearing wastewater using vermiculite expanded by microwave radiation and hydrogen peroxide and modified by chitosan. The adsorption properties of Hg(II) and the effects of pH, adsorption time and chitosan dosage were evaluated. At pH 6, the maximum removal rate was 96 % when 0.05 g/g chitosan was used for Hg(II) adsorption for 40 min. The kinetics and thermodynamics of Hg(II) adsorption on the modified vermiculite were also discussed. Under the optimum adsorption conditions, a pseudo-second-order kinetic model best described the reaction rate. Batch adsorption experiments conducted at different temperatures showed that the adsorption pattern followed the Freundlich isotherm model. The calculated thermodynamic parameters (ΔG, ΔH and ΔS) showed that the removal of Hg(II) using modified vermiculite was spontaneous and exothermic. These results proved the feasibility of using modified vermiculite to process mercury-bearing wastewater.

Keywords: Modified vermiculite, Mercury, Adsorption, Kinetics, Thermodynamics.

INTRODUCTION

With the vast developments in different industries, heavy metal pollution has emerged as one of the most important problems. Pollutants exceeding the environmental tolerance levels are usually not degradable in the natural environment[1,2]. Mercury is a pollutant that poses a threat to living organisms. The principal sources of mercury include coal-fired power plants, energy-saving light bulb, paper industries, mercury ores, battery, polyvinyl chloride (PVC) production, *etc*.[3,4]. Moreover, the chlor-alkali industry uses mercury as catalyst to produce PVC in China. Mercury discharge must be strictly controlled because this pollutant can heavily damage humans and animals through biomagnification in the biosphere and in the food chain.

The conventional treatments for the removal of mercury from wastewaters are precipitation, coagulation, reduction, solvent extraction, electrochemical separation through membranes, ion exchange and adsorption[5]. Among these methods, adsorption is the most effective and economic[6,7]. However, more natural and low-cost adsorbents need to be explore.

Vermiculite is an interstratified mineral consisting of phlogopite (or biotite) and vermiculite crystal layer. Vermiculite is widely available, easily handled and low cost. Vermiculite has unusual expanding property when rapidly heated[8]. Moreover, it has various properties, such as large specific surface area and good adsorption and ion exchange properties[9]. These

properties allow vermiculite be used to treat wastewater containing heavy metal ions and organic substance, *etc*. Several studies have focused on the adsorption of heavy metals by vermiculite[10-14].

Expanded vermiculite has higher cation exchange capacities and specific surface area than raw vermiculite. Increasing the multiple of expansion can improve the adsorption effect of vermiculite. Efforts have been devoted to develop methods that can improve the adsorption ability of raw vermiculite. Expanded vermiculite can be used to increase the specific surface area by multiple expansion and to improve the adsorption ability. Vermiculites can be exfoliated using chemical and thermal methods. Hydrogen peroxide is the most commonly used chemical modifier. Ucgul and Girgin[15] found that the maximum exfoliation value of phlogopite is 49-fold, which was obtained in 30 % hydrogen peroxide solution at room temperature. Obut and Girgin[16] reported a method using hydrogen peroxide to modify vermiculite.

Microwave heating has the advantages of short time, high efficiency and easy control. Thus, microwave heating has been widely used in vermiculite modification in recent years. Obut *et al*.[17] investigated the effects of microwave power and heating time on the exfoliation characteristics of vermiculites and found that the expansion multiple of vermiculite sample is 2.8. Kingman and Rowson[18] and Justo *et al*.[19] reported the effect of microwave.

Chitosan is a major component of crustacean shells and one of the most abundant biopolymers in nature[20]. Chitosan has superior adsorption ability for heavy metals because of its high content of amino groups[21]. As an adsorbent, chitosan can chelate with heavy metals. Chitosan has been broadly applied in water treatment. Many scholars reported that chitosan is a suitable biopolymer for the removal of metal ions from wastewater[22-25].

Chitosan is useful for the removal of metal ions. However, chitosan has many disadvantages, such as small density and slow sedimentation rate, causing difficulties in separating solids and liquids. Chitosan is difficult to contact with contaminants and loss easy in acidic solution. Thus, using chitosan to treat wastewater is costly.

In the present work, chitosan was used to modify expanded vermiculite to improve the adsorption capacity of vermiculite for mercury. This strategy reduces the cost and combines the high adsorption properties of expanded vermiculite and chitosan. The adsorption Hg(II) behaviour of the modified vermiculite was investigated, including the influencing factors of adsorption and the adsorption theory of thermodynamics and kinetics. The results of this study showed that the modified vermiculite adsorbent has potential applications in wastewater treatment.

EXPERIMENTAL

Raw vermiculite was obtained from Yuli, Xinjiang Province. Raw vermiculite was washed 10 times with deionized water, sieved to obtain particles approximately 5 mm in size, dried in an oven at 60 °C and then stored until use. The dried vermiculite was ground in a laboratory-type ball mill and then sieved to a size fraction < 0.15 mm (passed through # 100 sieve).

A stock Hg(II) solution (1000 mg/L) was prepared from mercuric chloride by dissolving appropriate amounts of $HgCl_2$ in 3 % HNO_3 and then diluted to the required concentration (ranging from 50 to 600 mg/L) with ultrapure water. All chemicals used in this work were of analytical grade, except for sodium hydroxide, potassium borohydride and nitric acid which were guaranteed reagent. Hydrochloric acid (0.1 mol/L) and NaOH (0.1 mol/L) were used for pH adjustment.

Preparation of expanded vermiculite: Raw vermiculite with an average size of 5 mm (5 g) was added into 50 mL of 25 % H_2O_2 aqueous solution with heating in a water bath (80 °C) for 60 min. After the treatment, the hydrated vermiculite was dried quickly by microwave radiation and then heated for 1 min in high power. The result of expansion ratio is 46.78. In addition, the dried vermiculite was ground in a laboratory-type ball mill and then sieved to a size fraction < 0.15 mm (passed through # 100 sieve).

Preparation of chitosan-modified vermiculite: Chitosan (0.1 g) was completely dissolved in 100 mL of 1 % (v/v) acetic acid solution. Then, 10 g of expanded vermiculite (combined with 25 % (m/m) H_2O_2 soaking and microwave heating modification) was dispersed into the as-prepared chitosan solution and stirred in a water bath at 50 °C for 2 h. Finally, the product was dried in an oven at 105 °C. The obtained sample was designated as 0.01 g/g chitosan-modified vermiculite. Using

the method given above, we prepared different mass percentages of chitosan-modified vermiculite.

Batch adsorption experiments: The stock Hg(II) solution (1000 mg/L) was diluted to 50 mg/L with ultrapure water. Then, 0.2 g of the modified vermiculite was added to a PTFE beaker with 30 mL of Hg(II) solutions of the desired concentration with continuous stirring. The suspensions were then filtered to determine Hg(II) concentration. The percent removal of Hg(II) was calculated as follows[26]:

$$\text{Removal} (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where C_i and C_f are the initial and final Hg(II) concentrations, respectively.

Batch experiments were conducted to study the effects of adsorption time, chitosan dosage and pH. The pH was adjusted to 4 to 8, the chitosan dosage ranged from 0 to 0.05 g/g and the adsorption time ranged from 10 min to 50 min under continuous shaking.

Batch adsorption kinetic and isotherms experiments were studied under optimum adsorption conditions. Adsorption kinetic experiments were collected at 10 to 50 min under optimum adsorption conditions and adsorption isotherm experiments were performed at different initial concentrations of Hg(II) (100, 200, 300, 400 and 500 mg/L) under optimum adsorption conditions.

Detection method: X-ray fluorescence (XRF) (AXIOS, Palmer naco instrument company, Holland) was used to analyze the elemental composition of the raw vermiculite and the X-ray diffraction (XRD) pattern (XD-3, Beijing Purkinje General Instrument Co., Ltd, China) at room temperature obtained for the structure of vermiculite. The concentration of Hg(II) ions was determined by double-pipe atomic fluorescence spectrometer (AFS-810, Beijing Titan Instrument Co., Ltd, China). pH meter (PHS-3B, Shanghai Hongyi instrument Co., Ltd, China) provided with incorporated thermal probe was used for pH measurements. The FT-IR spectra of vermiculite were recorded before and after adsorption using infrared spectrometer (AVATAR 360, Nicolet, USA) to obtain information on the nature of interactions between the functional groups of vermiculite and Hg(II) ions.

RESULTS AND DISCUSSION

Chemical composition and XRD of raw vermiculite: The chemical compositions (in weight percentage) of the raw vermiculite were determined by XRF analysis. The results are listed in Table-1. The XRD patterns for the raw vermiculite are presented in Fig. 1.

The XRD patterns of raw vermiculite (Fig. 1) indicated the coexistence of different materials of phlogopite and vermiculite. Reflections at d = 7.2 Å (002), 3.60 Å (004) and 2.88 Å (005) were the characteristic reflection of vermiculite. This reflection, together with those with *d*-spacing values of approximately 10.15, 3.36, 2.53 and 2.02 Å, corresponded to tophlogopite. The diffraction peaks of culsageeite were d = 3.6, 3.19, 2.09 Å, *etc.* indicating that the raw vermiculite had small amounts of vermiculite in its structure and vermiculite deposit in Weili, Xinjiang. Thus, the raw vermiculite is mainly composed

TABLE-1 CHEMICAL COMPOSITION OF THE RAW VERMICULITE						
Oxide	SiO_2	MgO	Al_2O_3	K_2O	Fe_2O_3	CaO	Na_2O
Wt. %	38.76	24.05	20.04	6.22	4.93	3.03	2.02

of hydrobiotite, a vermiculite-phlogopite inters-tratified mineral.

The XRD patterns of the modified vermiculite kept the characteristic peak of phlogopite. However, the characteristic peaks of vermiculite and culsageeite decreased and some diffractions disappeared. These results suggest that the main mineral is phlogopite. The intensity of the reflections was lower than raw vermiculite, indicating that the crystallinity of the modified vermiculite slightly declined and became amorphous.
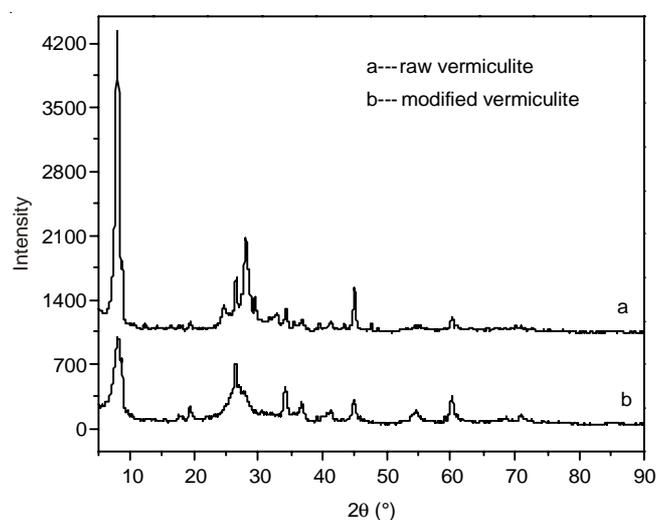
Fig. 1.   X-ray diffraction patterns of raw vermiculite and modified vermiculite

FT-IR analysis: The FT-IR spectra of raw vermiculite and modified vermiculite were collected to obtain information on the nature of interactions between the functional groups of the adsorbent and metal ions (Fig. 2).
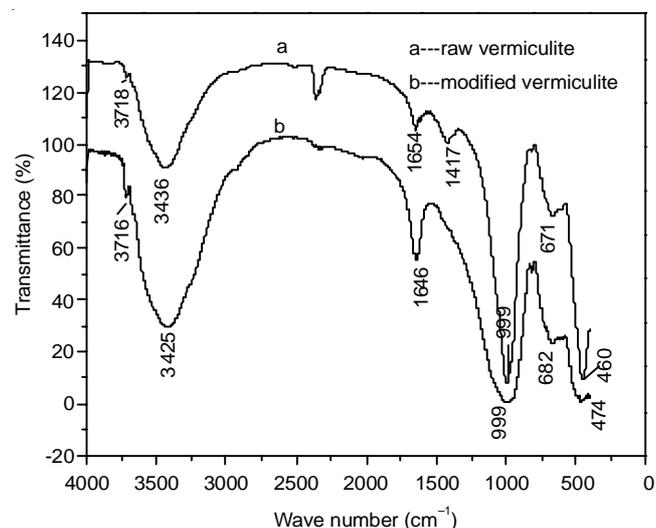
Fig. 2. FT-IR spectra of raw vermiculite and modified vermiculite

The adsorption band at 3718 cm^{-1} was attributed to the hydroxyl stretching vibration of phlogopite, which illustrates that the raw vermiculite contains phlogopite in phase. The main peak at 3436 cm^{-1} was assigned to the overlapping absorptions due to O-H stretching from water of hydration. Silanol groups Si-OH bonded and aluminum groups Al-OH bonded to the native matrix and Si-O-Si and Si-O-Al bonds appeared at 999 cm^{-1}. The peaks at 671 and 460 cm^{-1} were attributed to the stretching vibration of Al-O bonds[27]. The infrared spectrum of vermiculite showed that the peak at 1646 cm^{-1} can be assigned to hydration HOH vibration[21] and to the characteristic peak of NH_2. The peaks of the chitosan-modified vermiculite at 1646 and 3425 cm^{-1} both strengthened, indicating that chitosan was grafted onto the vermiculite. The basic framework of vermiculite structure was not destroyed after modification.

Influence factors of adsorption: The adsorption conditions of Hg(II) are as follows: Hg(II) solution concentration was 50 mg/L, Hg(II) solution volume was 30 mL and modified vermiculite amount was 0.2 g.

Effect of pH on removal rate: pH can affect not only the surface properties of the adsorbent but also the form of Hg(II) in a solution. Thus, pH is one of the major factors controlling adsorption. The effect of pH on the removal rate of Hg(II) onto modified vermiculite was studied by using different pH values (4 to 8). The results are demonstrated in Fig. 3. The removal rate considerably increased at pH 4 to 6. However, the removal rate for Hg(II) ions decreased to a certain degree when pH was higher than 6. The removal rate for Hg(II) ions peaked at 95 % at approximately pH 6.
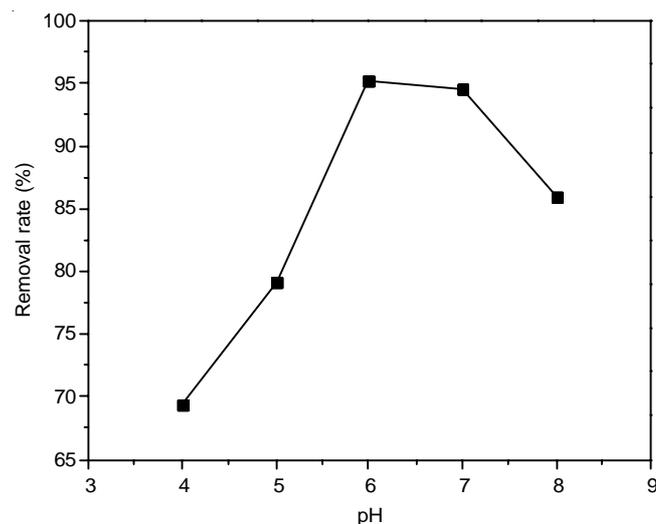
Fig. 3. Effect of pH on the removal efficiency of Hg(II) by the vermiculite

At low pH, H$^+$ concentration in the solution was higher, more protons can be available to protonate the active sites of vermiculite, the competition between H$^+$ and Hg(II) adsorption on vermiculite reduced the adsorption of Hg(II). As H$^+$

concentration decreased, the competition reduced, Hg(II) ion can take up the free active site, which increased the adsorption rate[3]. The adsorption of chitosan mainly occurred on amine -NH$_2$. At low pH, the chitosan molecular chain -NH$_2$ combined with H$^+$ in the solution and produced positively charged -NH$_3^+$, which made the chitosan gel surface positively charged. This phenomenon impeded the Hg(II) ions close to the molecular chains of chitosan and reduced the chelation with Hg(II), thereby reducing adsorption rate. When the solution pH gradually increased, the chelation of Hg(II) ions became stronger. When the pH was increased to more than 6, the concentration of hydroxyl ions increased and Hg(II) was hydrolyzed, which led to morphological changes and the formation of a stable hydroxyl complex and OH$^-$ also can occupy the active sites, thereby reducing adsorption rate. Basing on the experiment, we considered pH 6 to be the optimum value.

Effect of adsorption time on removal rate: Time is very important factor to study the adsorption equilibrium and practical applications. As shown in Fig. 4, the removal rate of Hg(II) ions increased rapidly with increasing time. After adsorption for 40 min, the sample reached adsorption equilibrium and then the removal rate increased very slowly with the experiment time. The percentage removal of Hg(II) ions was initially high because of the many vermiculite exchange sites available for the sorption of Hg(II) ions[28].

The adsorption of Hg(II) ion onto vermiculite is assumed to occur by a three-step model involving (1) mass transfer of Hg(II) ion from the bulk solution to the particle surface, (2) intraparticle diffusion and (3) adsorption at an interior site[29]. This finding indicates that the adsorption of the metal ions increases with time because Hg(II) ion is adsorbed on the surface of the modified vermiculite by static electric gravity and that the adsorption reduces because of Hg(II) ion migration and diffusion into the interlayer porosity internal of the modified vermiculite. The enhanced sorption of the metal ion with time may be due to the decrease in boundary layer resistance to mass transfer in the bulk solution and the increase in kinetic energy of the hydrated metal ion[30]. Thus, we considered 40 min to be the optimum reaction time.
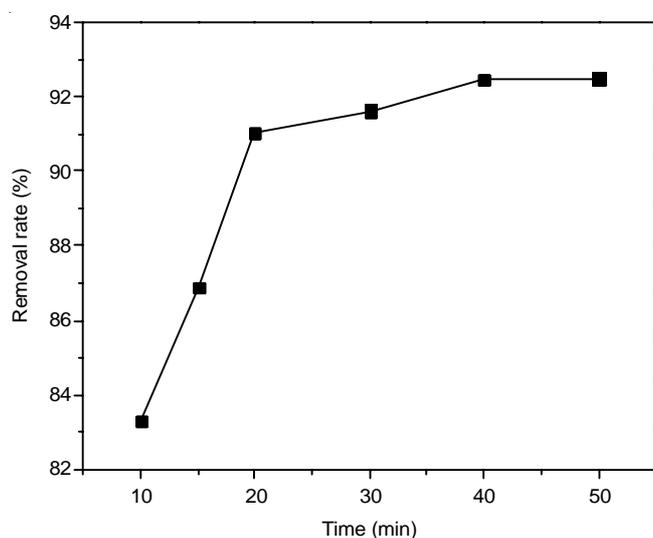
Fig. 4. Effect of time on the removal efficiency of Hg(II) by vermiculite

Effect of chitosan dosage on removal rate: The amount of chitosan affects the removal rate of Hg(II) ions. As shown in Fig. 5, the removal rate of Hg(II) ions increased with increasing chitosan dosage. The increase in removal rate was very slow when the mass per cent of chitosan and vermiculite was higher than 0.05. Thus, we speculated that the adsorption ability of chitosan-loaded vermiculite is related to the quantity of effective into the interlayer of chitosan. When the amount of chitosan did not exceed the vermiculite clay interlayer cation exchange capacity, chitosan increased with increasing modifier. The space for chitosan attachment may not be enough when the amount of chitosan was more than the cation exchange capacity. Thus, we considered 0.05 to be the optimum mass per cent of chitosan and vermiculite.
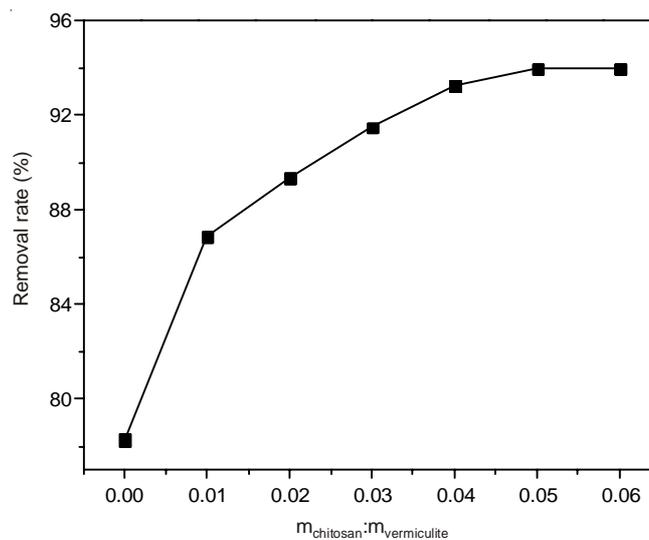
Fig. 5. Effect of chitosan dosage on the removal efficiency of Hg(II) by vermiculite

Adsorption kinetics: To investigate the rate law of Hg(II) adsorption with modified vermiculite, the kinetic data were analyzed using the pseudo-first-order and pseudo-second-order kinetic equations.

The equation for the pseudo-first-order is:

$$\log\left(q_e\text{-}q_t\right) = \log q_e - \frac{k_1 t}{2.303} \qquad (2)$$

The equation for the pseudo-second-order is:

$$\frac{dq_t}{dt} = k_2\left(q_e\text{-}q_t\right)^2 \qquad (3)$$

where q_e and q_t (both in mg/g) are the amounts of Hg(II) adsorbed at equilibrium and at time t (min), respectively and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants for adsorption of Hg(II)[31].

Eqn. 3 through integral obtains eqn. 4[32]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

The values of k_2 and qe were calculated from the slopes of the linear plots of t/q$_t$ *vs. t*.

Reaction kinetics models are shown in Figs. 6 and 7 and the data are listed in Table-2. Data analysis showed that the correlation coefficient R^2 of the pseudo-second-order model

was more than 0.999. These results showed that the pseudo-second-order kinetic model provided a better correlation for the adsorption of Hg(II) onto modified vermiculite than the pseudo-first-order model.
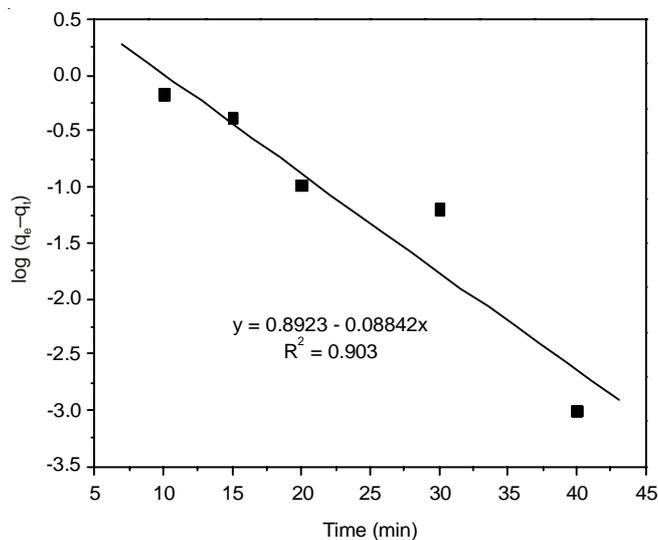
Fig. 6. Pseudo-first-order kinetic model
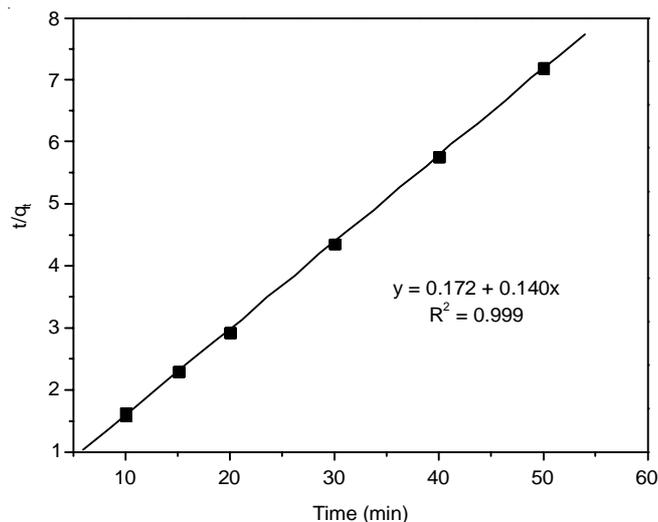
Fig. 7. Pseudo-second-order kinetic model

Adsorption isotherms: The Langmuir equation is the widely used two-parameter equation, commonly expressed as[33]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}K_L} + \frac{C_e}{Q_{max}} \qquad (5)$$

where Q_e and C_e are the amounts of Hg(II) adsorbed (mg/g) and equilibrium liquid-phase concentration (mg/L), respectively, K_L is a direct measure of the intensity of the sorption

(L/mg) and Q_{max} is a constant related to the area occupied by a monolayer of adsorbate, reflecting the adsorption capacity (mg/g). From the data of C_e/Q_e *vs.* C_e, Q_{max} and K_L can be determined from the slope and intercept.
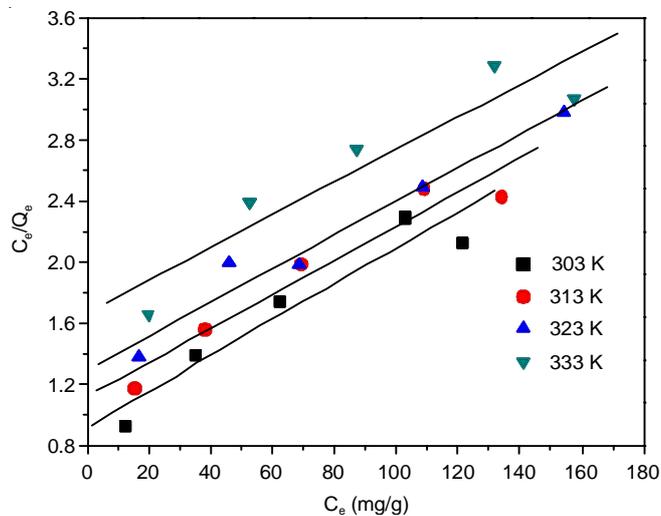
Fig. 8. Langmuir adsorption isotherms of Hg(II) on the vermiculite at different temperatures

The Freundlich adsorption isotherm represents the relationship between the amount of metal adsorbed per unit mass of the adsorbent Q_e and the concentration of the metal in solution at equilibrium. The Freundlich equation is commonly expressed as[34]:

$$\log Q_e = \frac{1}{n}\log C_e + \log K_F \qquad (6)$$
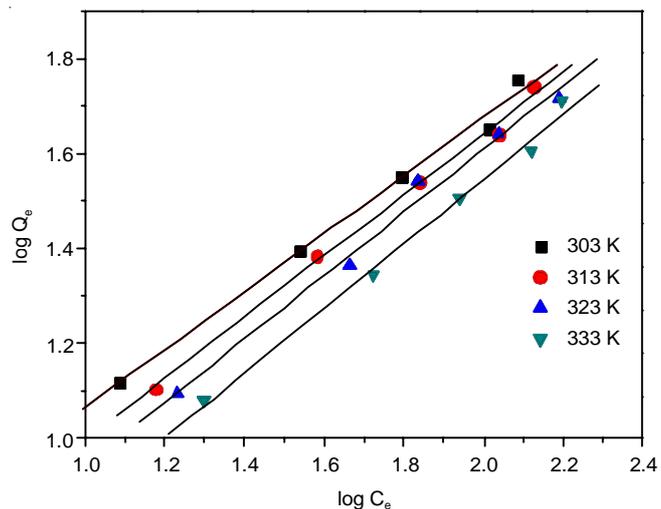
Fig. 9. Freundlich isotherms of Hg(II) on the vermiculite at different temperatures

TABLE-2 PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER PARAMETERS FOR THE ADSORPTION OF Hg(II) ONTO MODIFIED VERMICULITE					
Pseudo-first-order			Pseudo-second-order		
q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (mg^{-1} min^{-1})	R^2
7.80	0.204	0.903	7.14	0.114	0.999

where K_F [(mg/g)(L/mg)$^{1/n}$] and n (dimensionless) are constants incorporating all factors affecting the adsorption process, such as adsorption capacity and intensity, respectively. The values of n and K_F were calculated from the slope and intercept of the plot of log Q_e *vs.* log C_e.

Using the slope and the intercept of regression analysis of the linearized isotherms of Freundlich and Langmuir, we determined the sorption constants (K_F, n and Q_{max}, K_L) and correlation coefficients (R^2). The parameters of Freundlich and Langmuir equations at different temperatures are summarized in Table-3. The data showed better compliance with the Freundlich adsorption isotherm than with the Langmuir adsorption isotherm. The Freundlich constant K_F reflected the relative adsorption capacity of the adsorbent[35]. The Freundlich constant n is a measure of heterogeneity of adsorbent surface and relative intensity of adsorbent. As shown in Table-3, K_F decreased with increasing temperature, indicating that the adsorption processes were exothermic and that the increase in temperature went against adsorption. Veli and Alyuz[36] reported that the adsorption is linear, chemical, or physical when n is equal to unity, below unity, or above unity, respectively. Xiong and Yao[37] reported that adsorption is easy to proceed when n is more than 1, which represents the favorable adsorption condition. The general rule is that the exponent $1 < n < 10$ represents beneficial adsorption[38]. As shown in Table-3, n is more than 1, suggesting that the adsorption is physical and easy to proceed.

Thermodynamics parameters: Thermodynamic analysis revealed useful information on the adsorption process of Hg(II) on modified vermiculite from the aspect of energy change. The main thermodynamic parameters are given below.

Enthalpy change of adsorption (ΔH): ΔH during adsorption could be calculated according to Van't Hoff equation[38]. It can be obtained by the following eqn. 7:

$$\ln C_e = \frac{\Delta H}{RT} - \ln K_0 \qquad (7)$$

where C_e is the equilibrium concentration under given adsorption capacity; R is ideal gas constant [8.314 J/(mol K)]; T is degree Kelvin (K) ; K_0 is constant; and ΔH is the enthalpy change of equivalent adsorption (KJ/mol). ΔH would be calculated by rectilinear lope drawn by $\ln C_e$ *vs.* 1/T. The results are shown in Fig. 10.
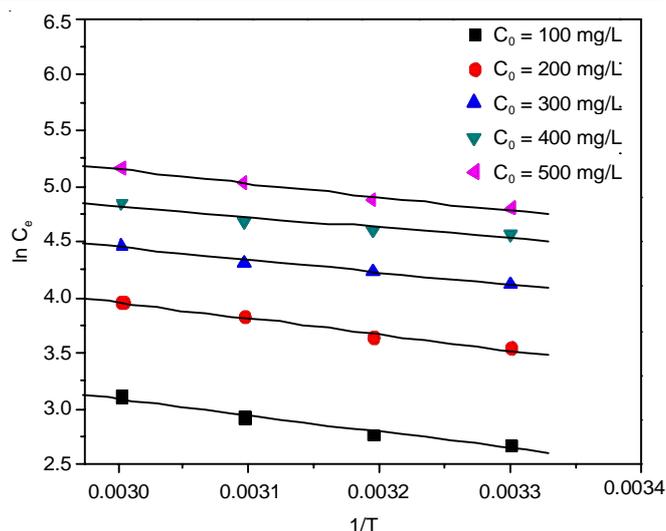
Fig. 10. Plots of ln C_e *vs.* 1/T

Adsorption free energy change (ΔG): Freundlich equation was selected and the concentration was low, suggesting that Q_e was not related to ΔG. Adsorption free energy change was evaluated using the following eqn. 8[38]:

$$\Delta G = -nRT \qquad (8)$$

where n is the coefficient of the Freundlich isothermal equation, R is the gas constant and T is the absolute temperature (K).

Adsorption entropy change (ΔS): ΔS could be calculated in terms of Gibbs-Helmholtz equation based on the gained ΔH and ΔG. It can be obtained by the following eqn. (9)[39]:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (9)$$

The negative values of ΔH indicate that the adsorption process is exothermic and the values (10 to 30 kJ/mol) demonstrate that the adsorption process is a physisorption process[39]. The negative values of ΔG indicate that the process is spontaneous. A similar result was found by Liu *et al.*[40], who studied lead(II) adsorption on vermiculite. In this study, the negative values of ΔG indicate that the sorption process is feasible and that the adsorption becomes more spontaneous with increasing temperature. The absolute values of ΔG for modified vermiculate is lower than 20 kJ/mol, suggesting the physisorption

TABLE-3
ADSORPTION PARAMETERS OF THE Hg(II) ON THE MODIFIED VERMICULITE AT DIFFERENT TEMPERATURES

Temperature (K)	Langmuir constants			Freundlich constants		
	R^2	Q_m (mg/g)	K_L (10^{-3})	R^2	n	K_F
303	0.96	110	8.47	0.99	1.46	2.07
313	0.96	110	7.54	0.99	1.46	1.87
323	0.98	100	6.99	0.99	1.43	1.58
333	0.99	100	5.61	0.99	1.41	1.29

TABLE-4
THERMODYNAMICS PARAMETERS OF ADSORPTION

C_0 (mg/L)	ΔH (KJ mol^{-1})	ΔG (KJ mol^{-1})				ΔS (J mol^{-1} K^{-1})			
		303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K
100	-12.23					-28.28	-27.04	-26.06	-25.02
200	-12.13					-27.93	-26.72	-25.75	-24.72
300	-9.20	-3.67	-3.77	-3.81	-3.90	-18.27	-17.37	-16.69	-15.93
400	-7.85					-13.79	-13.03	-12.48	-11.85
500	-10.38					-22.17	-21.14	-20.34	-19.48

nature of present adsorption process. The ΔG valued changed slightly with increasing solution temperature from 303 to 333 K. This result indicates the existence of entropy compensation[41] and the slight effect of temperature.

The negative value of ΔS suggests a decreased randomness at the solid/solution interface during the adsorption of Hg(II) on the modified vermiculite. ΔS is usually negative because ions in solution have more freedom of motion than the ones attached to a surface[42]. Absolute entropy values slightly decrease with increasing temperature; this phenomenon is more marked with increasing coverage[39]. It also indicates that Hg(II) in the adsorbent surface is in a much less chaotic distribution compared with the relatively ordered state of aqueous solution.

Comparison of Hg(II) adsorption capacities by various adsorbents: The maximum adsorption capacities of various adsorbents to Hg(II) are compared in Table-5. Although the data may or may not represents equivalent. It still can provide a useful comparison regarding decision of selection of suitable adsorbent. The results showed that modified vermiculite has relatively high adsorption capacity to Hg(II), reflecting the modified vermiculite is a promising adsorbent in removing Hg(II) from wastewater.

TABLE-5
COMPARISON OF Hg(II) ADSORPTION CAPACITIES
BY VARIOUS ADSORBENTS

Adsorbent	Q_m (mg/g)	References
Adulsa leaves powder	107.3	3
Malt spent rootless	50	43
Modified vermiculite	110	Present study
AEPE-montmorillonite	46.1	44
GLA-chitosan	75.5	45
AEPE-hectorite	54.7	44
Walnut shell	151.51	46

Conclusion

Modified vermiculite can be used to treat wastewater contaminated by Hg(II). This study focused on the optimum adsorption conditions of Hg(II) removal using the modified vermiculite from aqueous solution. The optimum adsorption conditions are as follows: pH 6, chitosan amount of 0.05 g/g, treatment time of 40 min. Adsorption kinetic data were analyzed using the pseudo-first-order and pseudo-second-order models. The results showed that the process can be better described by the pseudo-second-order kinetic model than the pseudo-first-order model. Adsorption equilibrium was better described by the Freundlich model than the Langmuir isotherm model. The calculated thermodynamic parameters (ΔG, ΔH and ΔS) showed that the removal of Hg(II) by modified vermiculite was spontaneous, exothermic and feasible.

The results of this study show that the considerable adsorption capacity of the modified vermiculite makes it an effective adsorbent for the removal of Hg(II) ions from wastewater. In addition, vermiculite is feasible to be used for industrial wastewater treatment because of its abundance and low cost. Based on the study of adsorption kinetics and thermodynamics, it can enrich the adsorption theory. This study provides a theoretical basis for the removal of Hg(II) ions.

REFERENCES

1. C.K. Jain and M.K. Sharma, *Water Air Soil Pollut.*, **137**, 1 (2002).
2. Y.C. Sharma, V. Srivastava, V.K. Singh, S.N. Kaul and C.H. Weng, *Environ. Technol.*, **30**, 583 (2009).
3. M. Aslam, S. Rais, M. Alam and A. Pugazhendi, *Eur. J. Chem.*, **2013**, 1 (2013).
4. S. Sophie Beulah and K. Muthukumaran, *Asian J. Chem.*, **22**, 3601 (2010).
5. R.S. Juang and H.J. Shao, *Water Res.*, **36**, 2999 (2002).
6. W. Jiang, M. Pelaez, D.D. Dionysiou, M.H. Entezari, D. Tsoutsou and K. O'Shea, *Chem. Eng. J.*, **222**, 527 (2013).
7. M. Xu, H.J. Wang, D. Lei, D. Qu, Y.J. Zhai and Y.L. Wang, *J. Environ. Sci. (China)*, **25**, 479 (2013).
8. C. Marcos and I. Rodríguez, *Appl. Clay Sci.*, **48**, 492 (2010).
9. M.S. Wang, L.B. Liao, X.L. Zhang, Z.H. Li, Z.G. Xia and W.D. Cao, *Clays Clay Miner.*, **59**, 459 (2011).
10. M.G. Da Fonseca, M.M. De Oliveira, L.N. Arakaki, J.G. Espinola and C. Airoldi, *J. Colloid Interface Sci.*, **285**, 50 (2005).
11. A.C. Vieira dos Santos and J.C. Masini, *Appl. Clay Sci.*, **37**, 167 (2007).
12. T. Mathialagan and T. Viraraghavan, *Sep. Sci. Technol.*, **38**, 57 (2003).
13. T. Lee, *Water Air Soil Pollut.*, **223**, 3399 (2012).
14. Y. Liu, D. Xiao and H. Li, *Sep. Sci. Technol.*, **42**, 185 (2007).
15. E. Ucgul and I. Girgin, *Turk. J. Chem.*, **26**, 431 (2002).
16. A. Obut and I. Girgin, *Miner. Eng.*, **15**, 683 (2002).
17. A. Obut, I. Girgin and A. Yörükoglu, *Clays Clay Miner.*, **51**, 452 (2003).
18. S.W. Kingman and N.A. Rowson, *J. Microwave Power Electromagnet. Energy*, **35**, 144 (2000).
19. A. Justo, J.L. Perez-Rodriguez and P.J. Sanchez-Soto, *J. Therm. Anal. Calorim.*, **40**, 59 (1993).
20. R.S. Vieira and M.M. Beppu, *Water Res.*, **40**, 1726 (2006).
21. K. Zhang, J. Xu, K.Y. Wang, L. Cheng, J. Wang and B. Liu, *Polym. Degrad. Stab.*, **94**, 2121 (2009).
22. H. Cui, Y. Qian, Q. Li, Q. Zhang and J.P. Zhai, *Chem. Eng. J.*, **211-212**, 216 (2012).
23. A.J. Varma, S.V. Deshpande and J.F. Kennedy, *Carbohydr. Polym.*, **55**, 77 (2004).
24. F.C. Wu, R.L. Tseng and R.S. Juang, *J. Environ. Manage.*, **91**, 798 (2010).
25. E. Guibal, *Sep. Purif. Technol.*, **38**, 43 (2004).
26. A. Sari and M. Tuzen, *Sep. Sci. Technol.*, **43**, 3563 (2008).
27. V.C. Farmer, Mineralogical Society, London (1974).
28. F. Gode and E. Pehlivan, *J. Hazard. Mater.*, **136**, 330 (2006).
29. Y.S. Choi and J.H. Cho, *Environ. Technol.*, **17**, 1169 (1996).
30. M.J. Horsfall and A.A. Abia, *Water Res.*, **37**, 4913 (2003).
31. J. Pradhan, S.N. Das and R.S. Thakur, *J. Colloid Interf. Sci.*, **217**, 137 (1999).
32. Y.S. Ho and G. McKay, *Process Biochem.*, **34**, 451 (1999).
33. W.T. Tsai, C.W. Lai and K.J. Hsien, *J. Colloid Interf. Sci.*, **263**, 29 (2003).
34. C.O. Ijagbemi, M.H. Baek and D.S. Kim, *J. Hazard. Mater.*, **166**, 538 (2009).
35. Q. Li, Q.Y. Yue, Y. Su, B.Y. Gao and H.J. Sun, *Chem. Eng. J.*, **158**, 489 (2010).
36. S. Veli and B. Alyuz, *J. Hazard. Mater.*, **149**, 226 (2007).
37. C.H. Xiong and C.P. Yao, *J. Hazard. Mater.*, **166**, 815 (2009).
38. Z.W. Zhao, X.Y. Xu, X.Y. Chen, G.S. Huo, A.L. Chen, X.H. Liu and H. Xu, *T. Nonferr. Metal. Soc.*, **22**, 686 (2012).
39. R.A. Garcia-Delgado, L.M. Cotoruelo-Minguez and J.J. Rodriguez, *Sep. Sci. Technol.*, **27**, 975 (1992).
40. Y. Liu, D. Xiao and H. Li, *Sep. Sci. Technol.*, **42**, 185 (2007).
41. X.L. Du, Q.P. Yuan and Y. Li, *Chem. Eng. Process.*, **47**, 1420 (2008).
42. K. Laidler and J. Meiser, Houghton Mifflin Company, Boston (1995).
43. V.A. Anagnostopoulos, I.D. Manariotis, H.K. Karapanagioti and C.V. Chrysikopoulos, *Chem. Eng. J.*, **213**, 135 (2012).
44. T. Phothitontimongkol, N. Siebers, N. Sukpirom and F. Unob, *Appl. Clay Sci.*, **43**, 343 (2009).
45. R.S. Vieira and M.M. Beppu, *Colloid Surf. A*, **279**, 196 (2006).
46. M. Zabihi, A. Ahmadpour and A.H. Asl, *J. Hazard. Mater.*, **167**, 230 (2009).